



**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.

Xiang Li

University of Maryland, Baltimore County

Andrej Grubisic

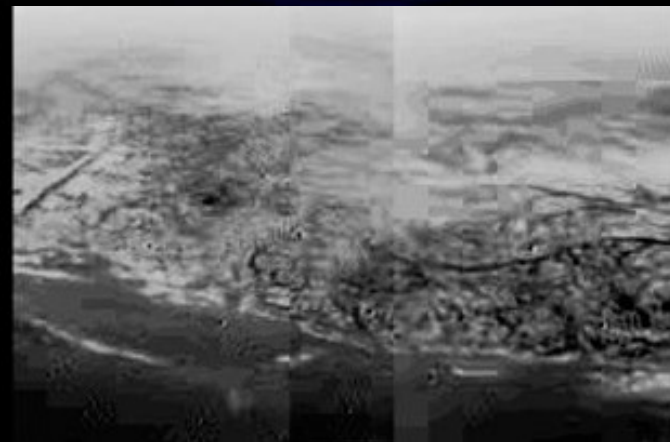
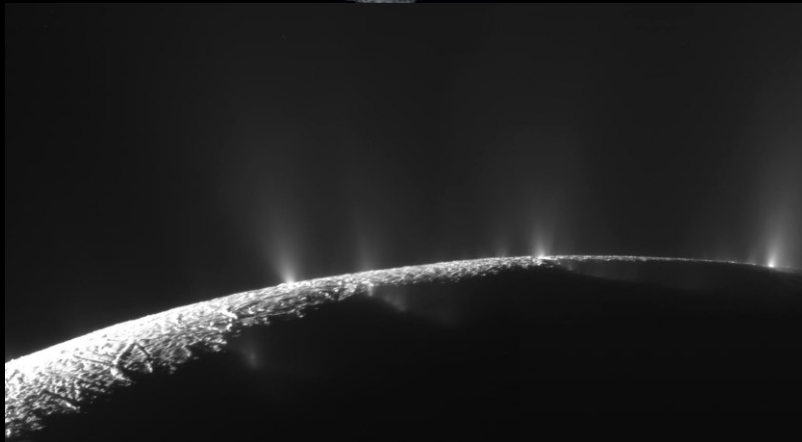
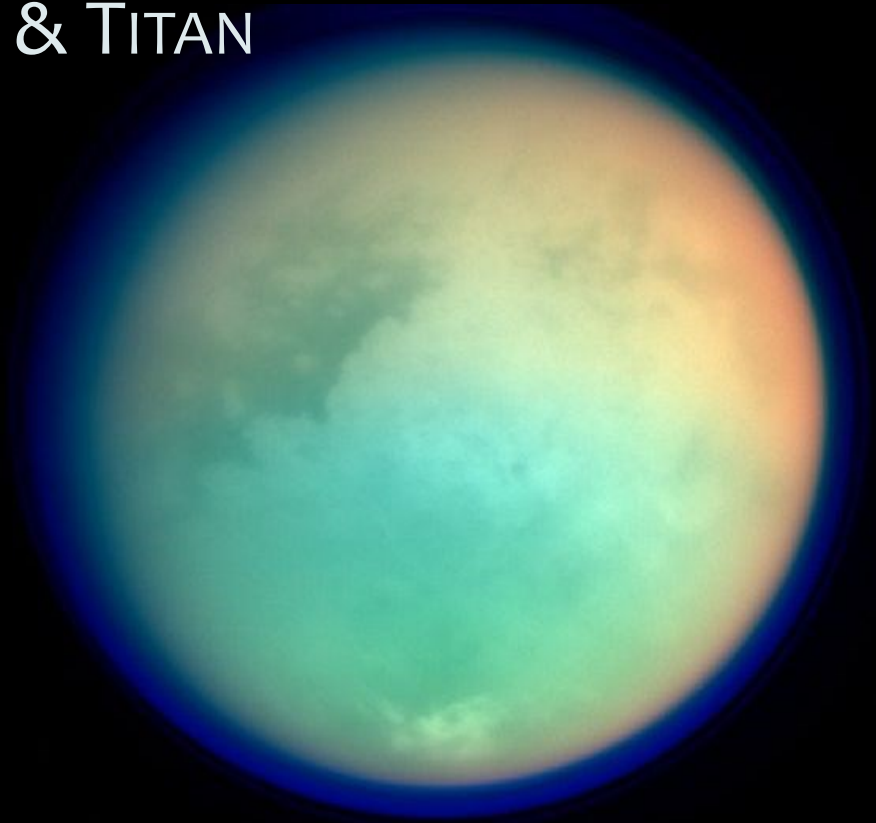
University of Maryland, College Park

Kyle Uckert

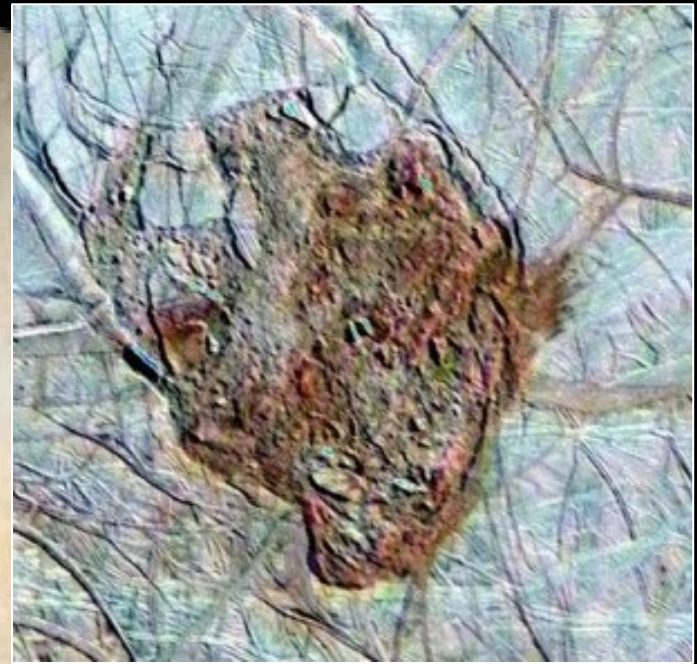
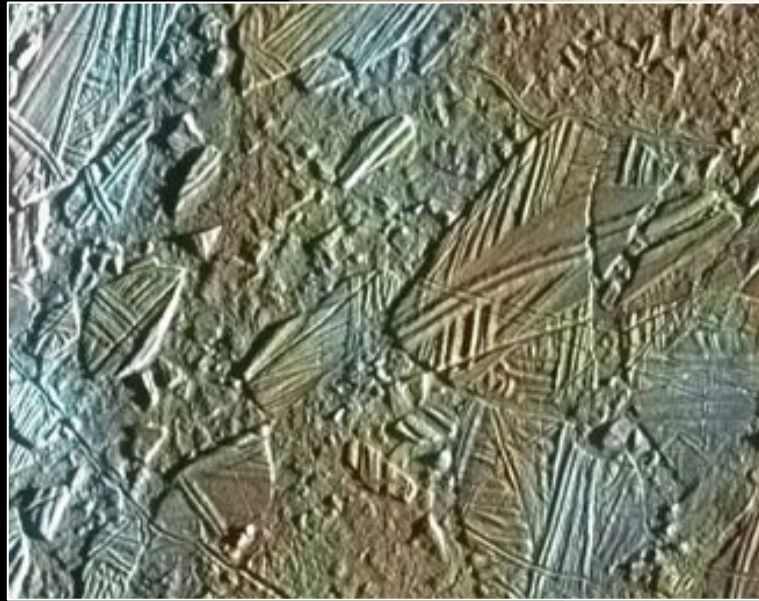
New Mexico State University

SOLAR SYSTEM DESTINATIONS...
THAT ARE JUST BEGGING TO BE ANALYZED!

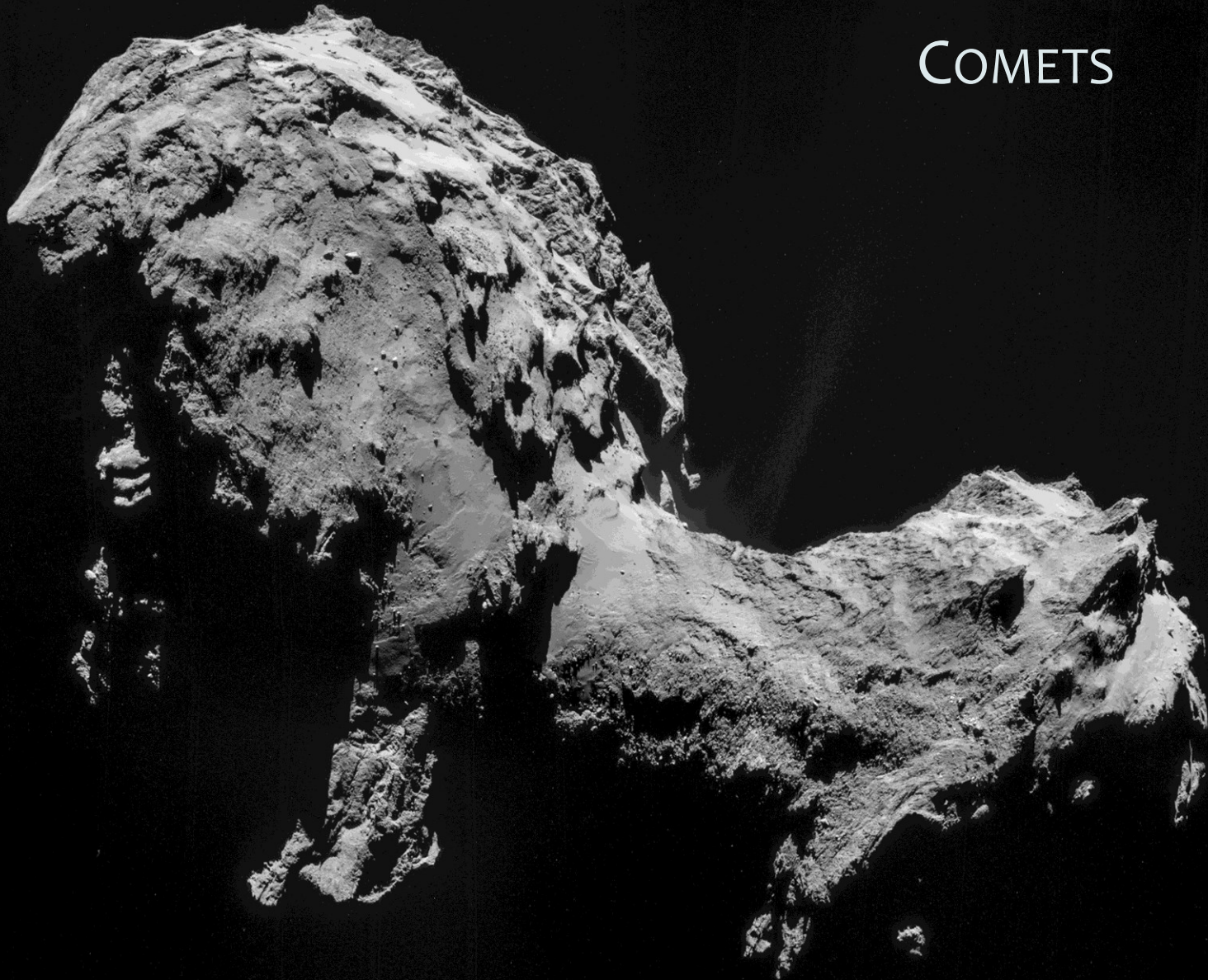
ENCELADUS & TITAN



EUROPA

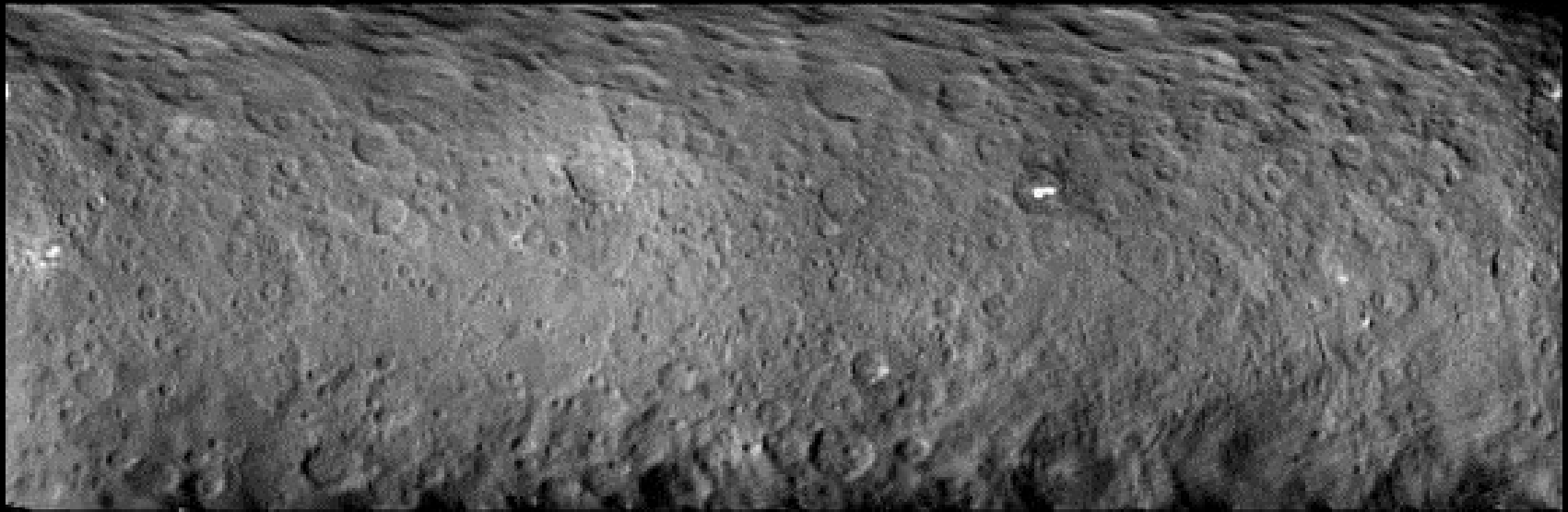


COMETS

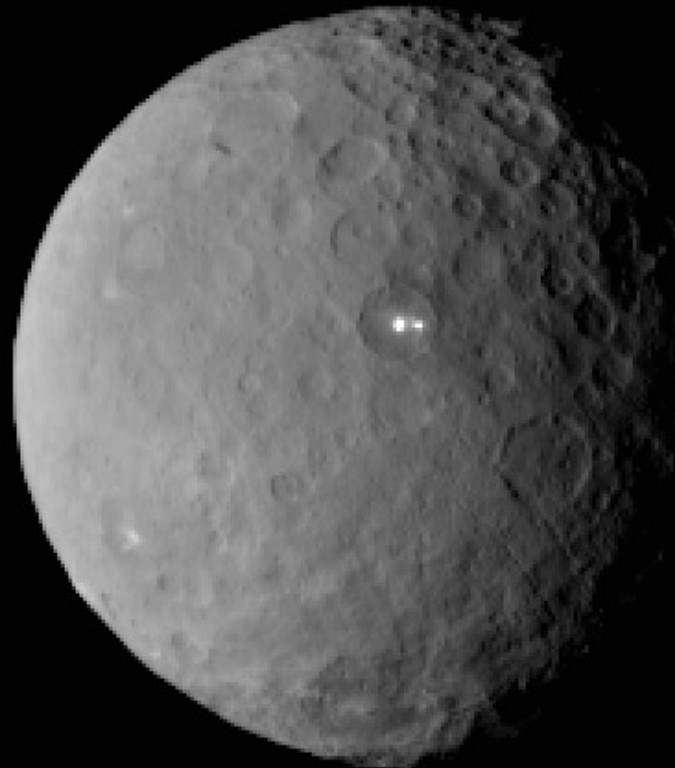


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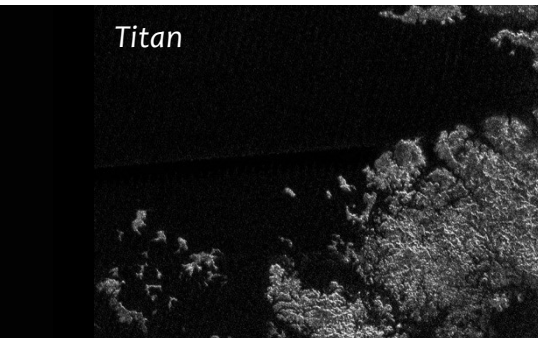
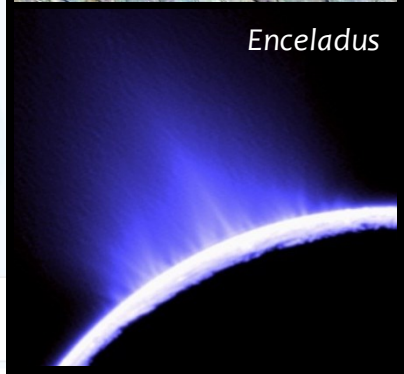
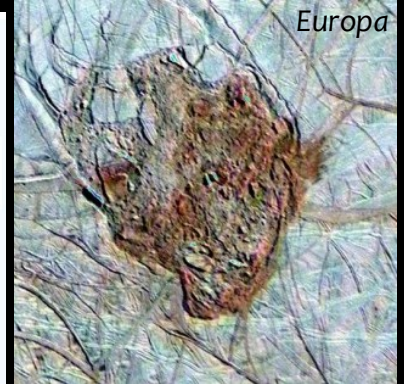
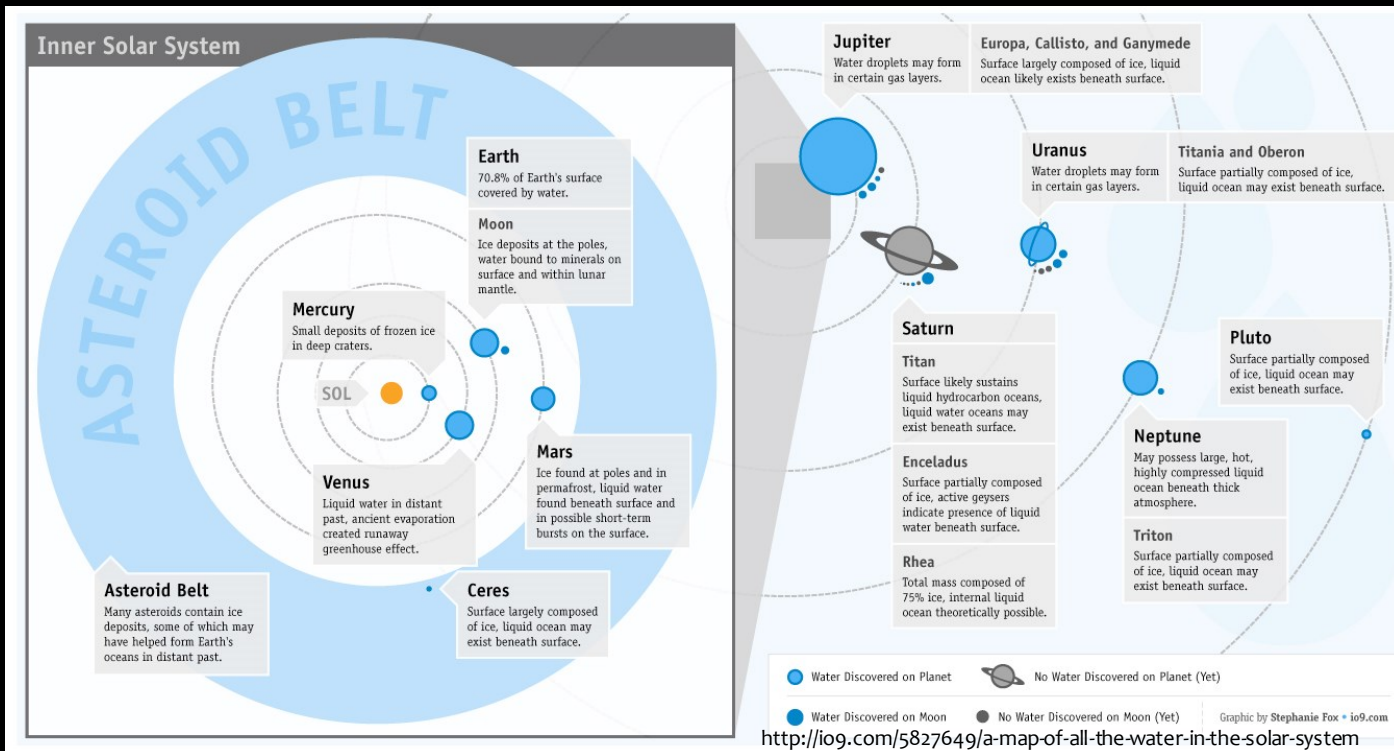
(E.G., 67P CHURYUMOV-GERASIMENKO)



CERES



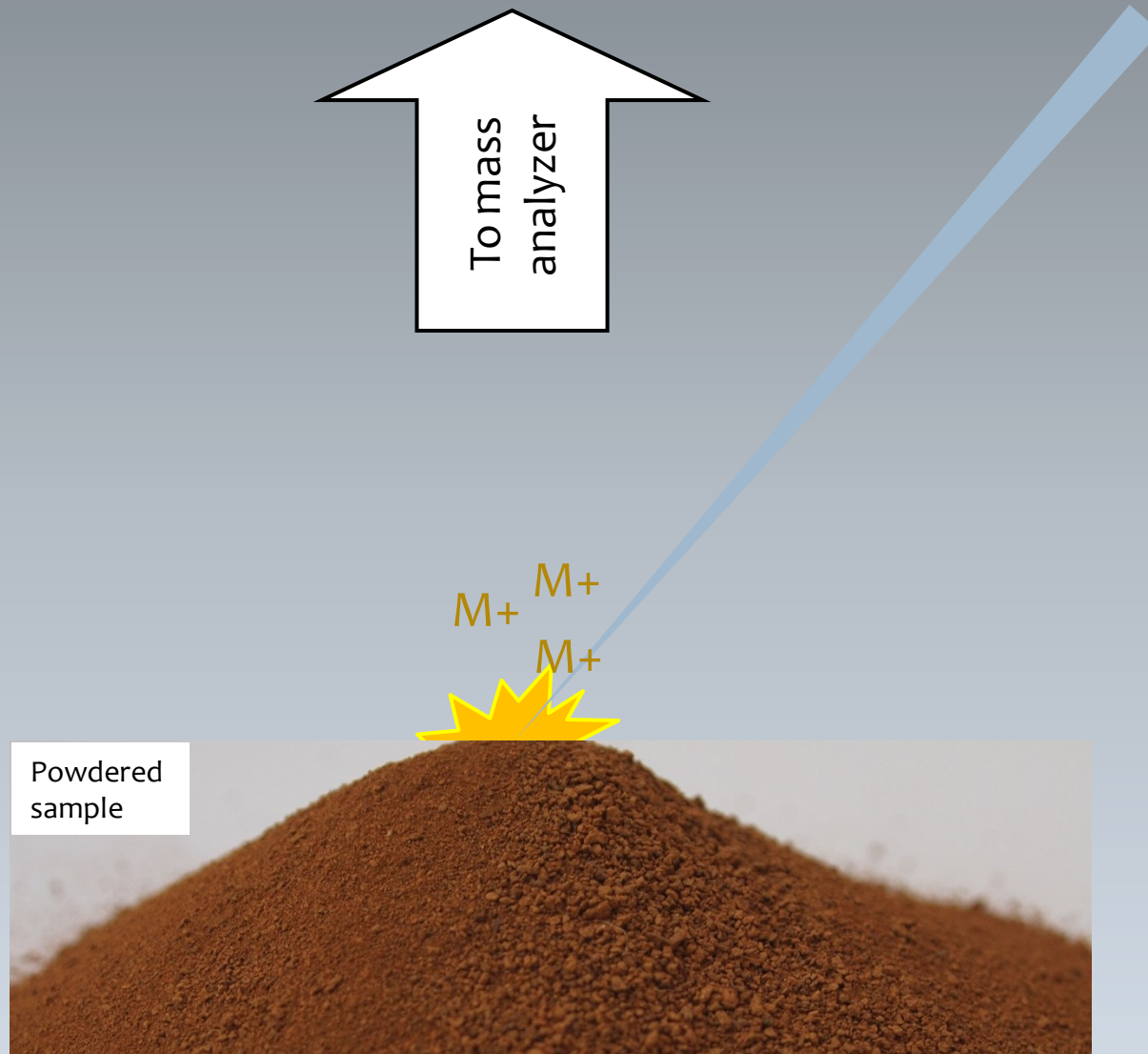
WHAT DO THESE BODIES HAVE IN COMMON? VOLATILES, INCLUDING WATER!



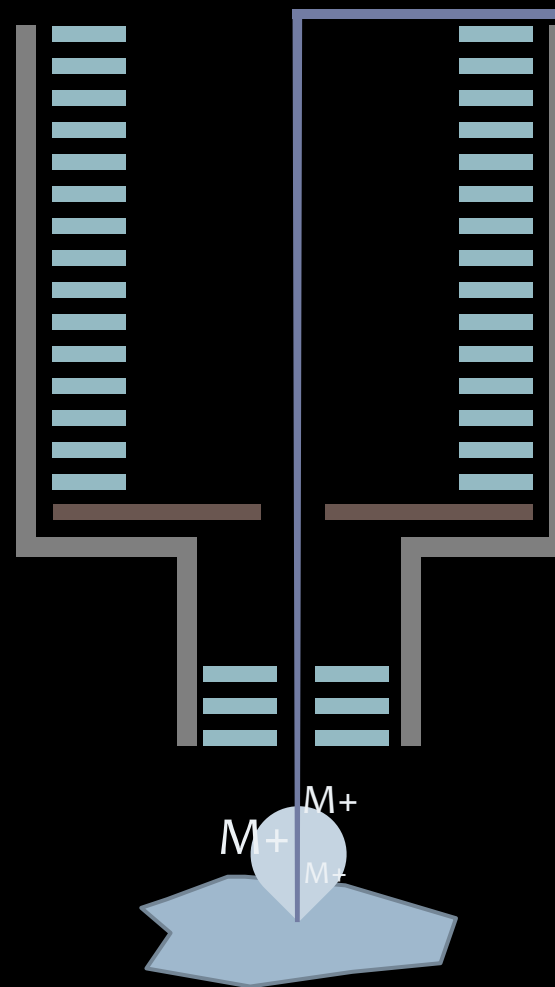
WHY MASS SPECTROMETRY FOR PLANETARY MISSIONS?

- ‘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

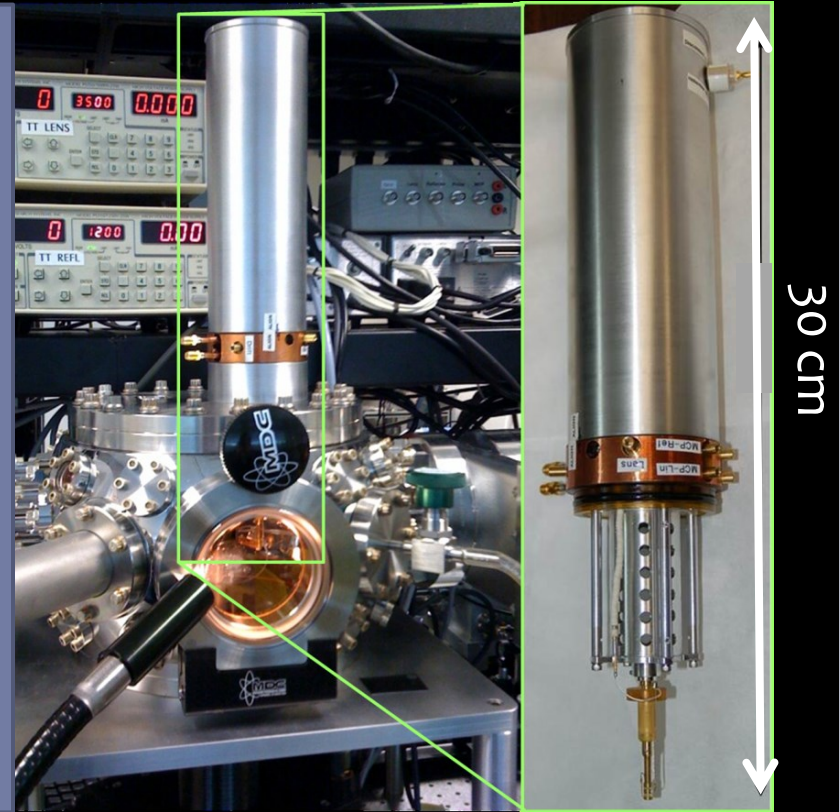


Commercial LD-TOF-MS (or MALDI) is a gold-standard technique for the analysis over a wide range of molecular weight, including large biomolecules



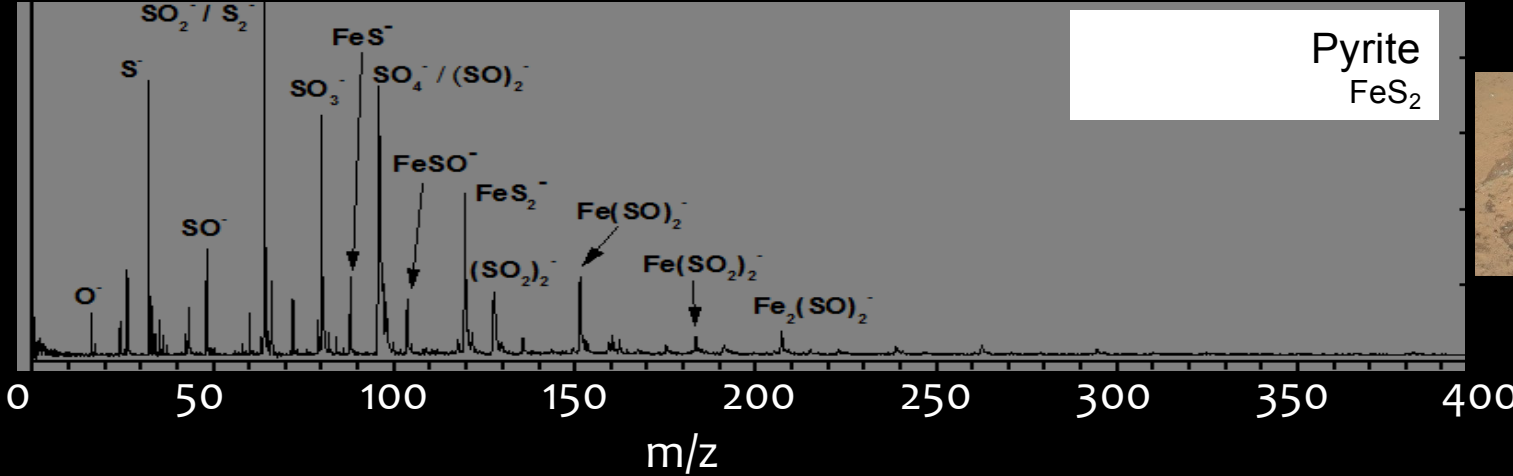
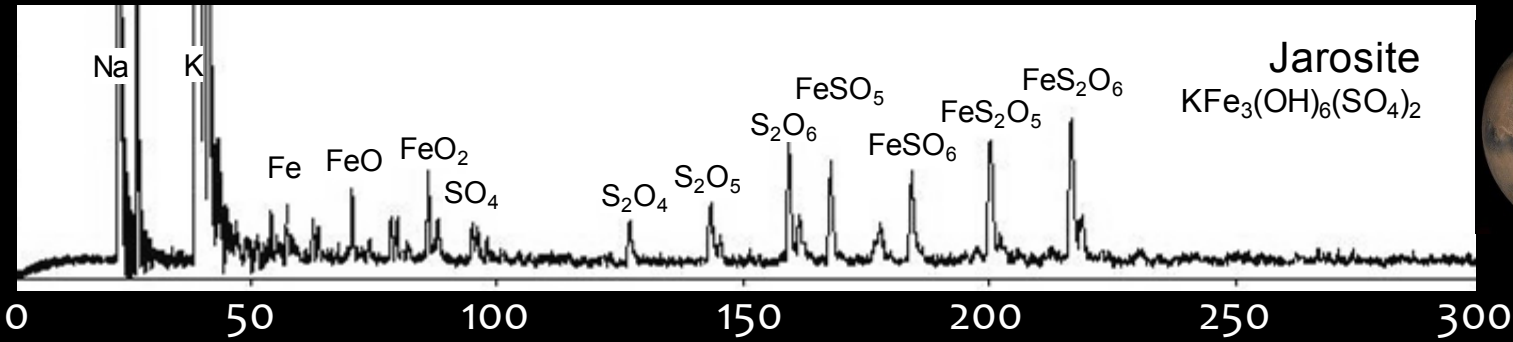
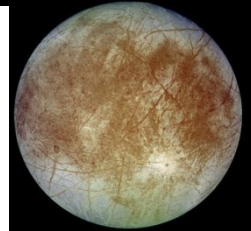
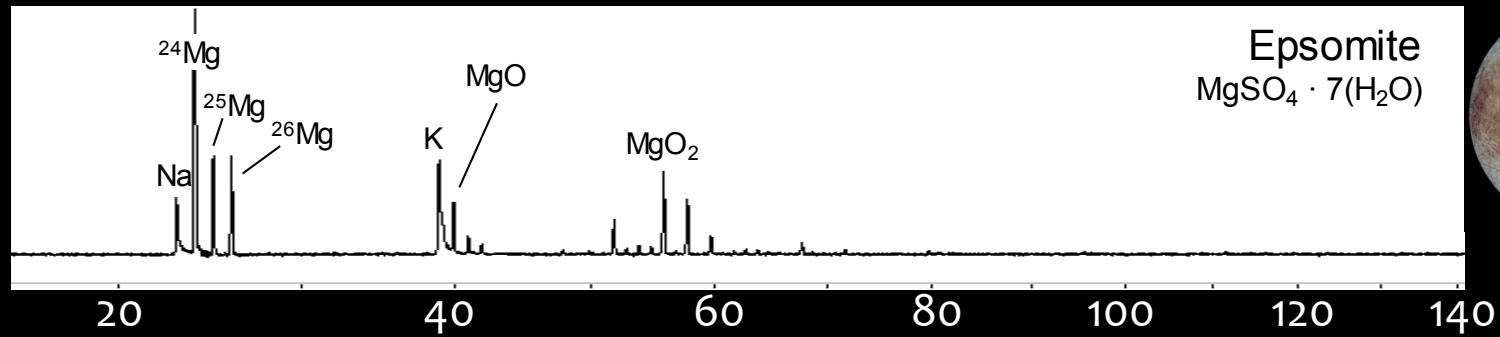
LD-TOF-MS as a compact instrument is capable of analyzing broadband composition directly from a solid sample

- 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 & $^{12}\text{C}/^{13}\text{C}$ patterns

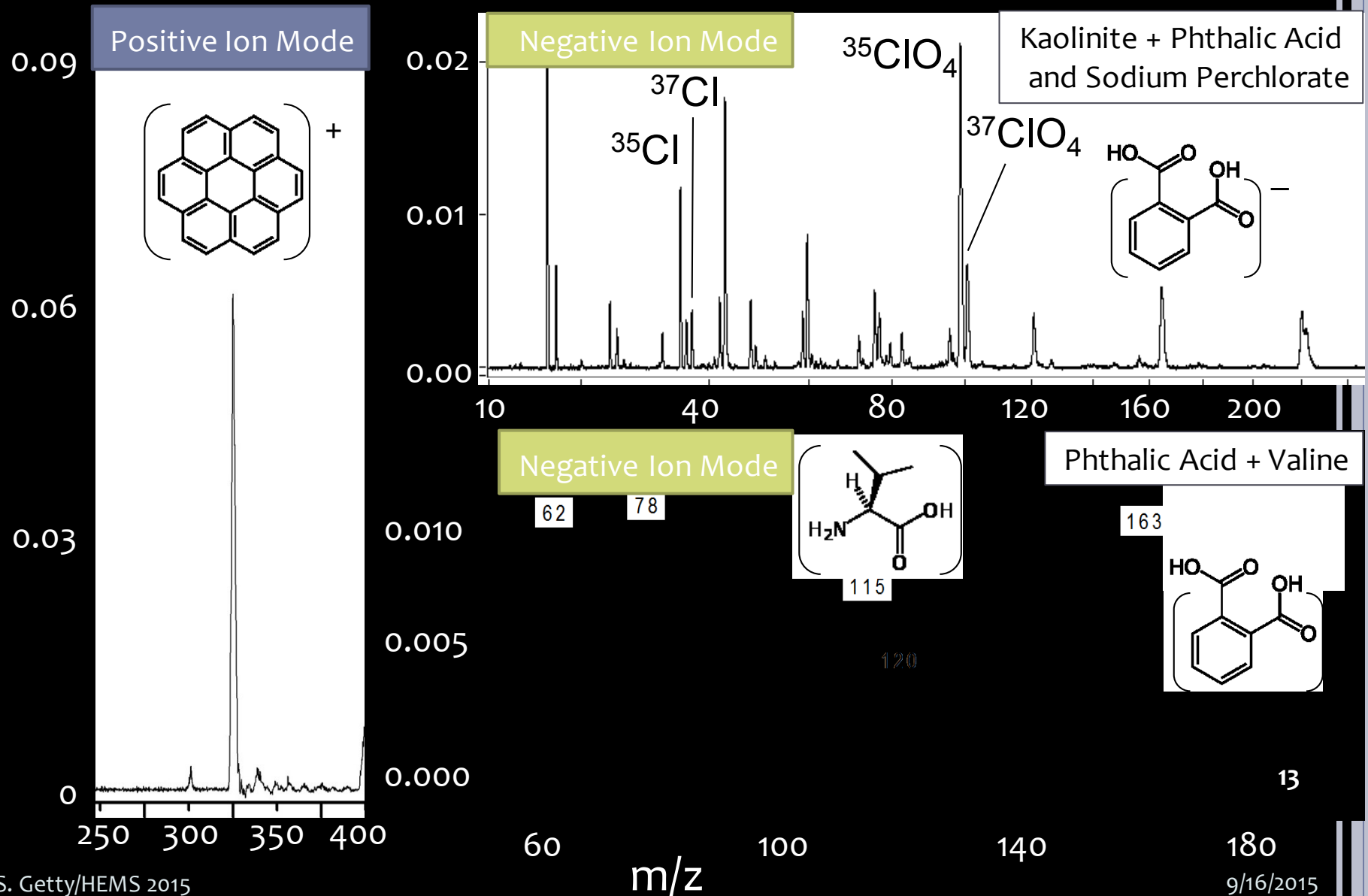


DUAL POLARITY ION MODE: INORGANIC COMPOSITION

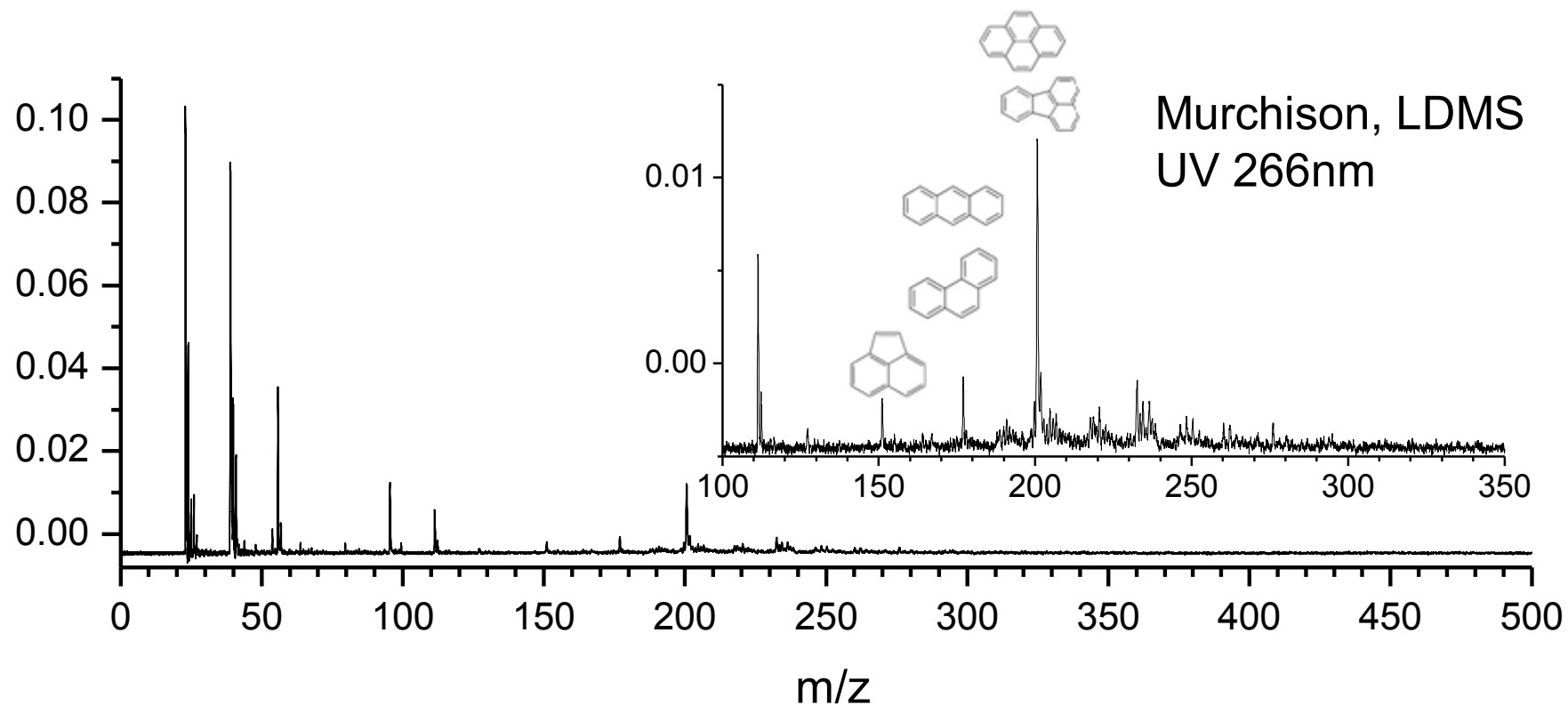
SEDIMENTARY AND AQUEOUSLY ALTERED MINERALS



COMPLEMENTARY POSITIVE AND NEGATIVE ION DETECTION: DETECTING ORGANICS ACROSS CLASSES



BUT IN REALITY WE COULD GET A SPECTRUM LIKE...

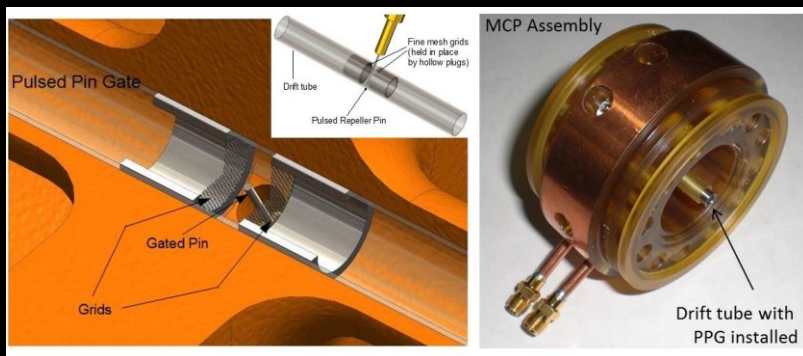
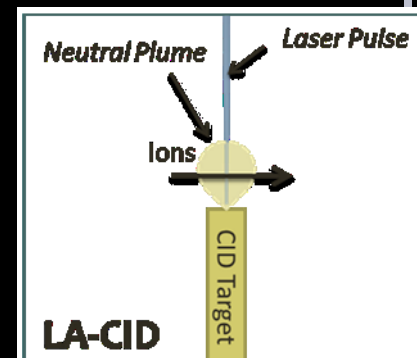
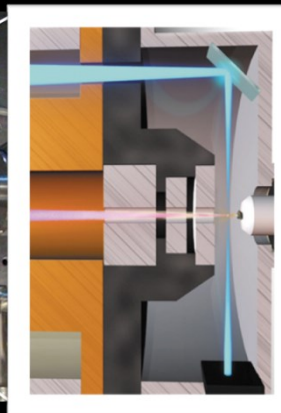
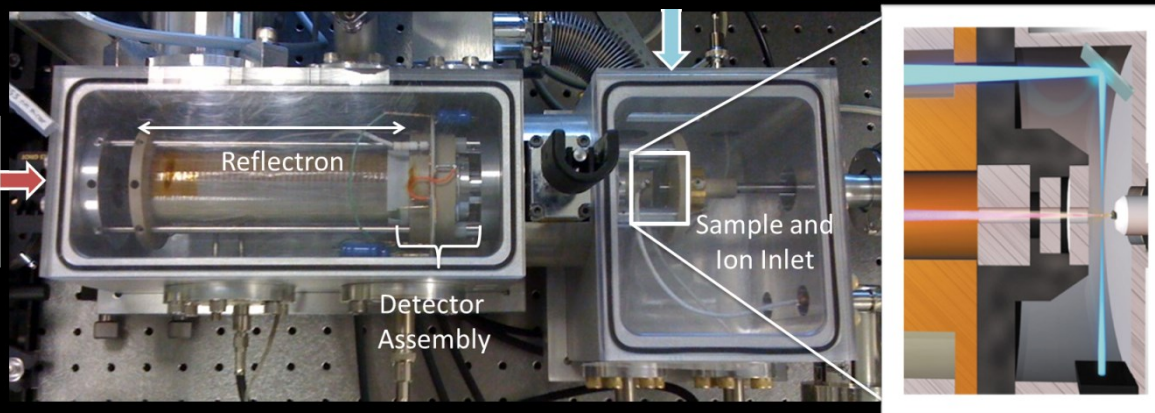


TANDEM TWO-STEP LASER MASS SPECTROMETER

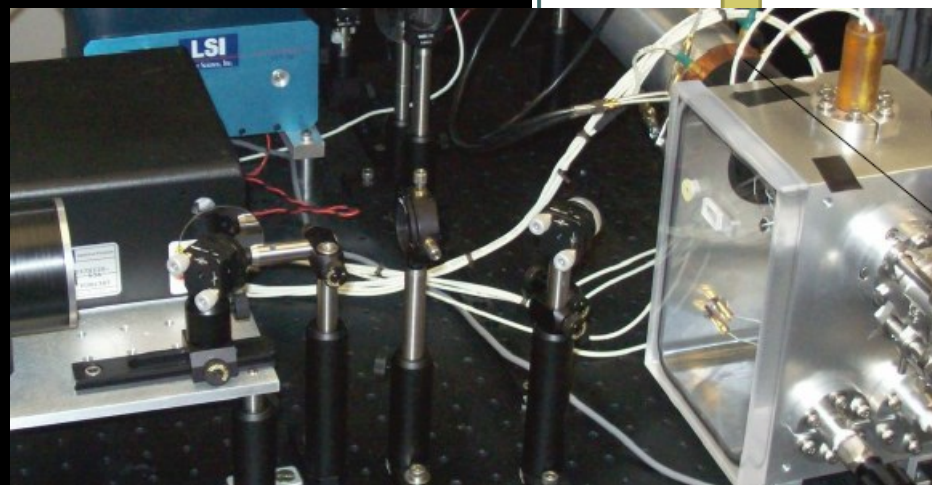
Two-Step LDI

Ionization
Pulse

Desorption
Pulse



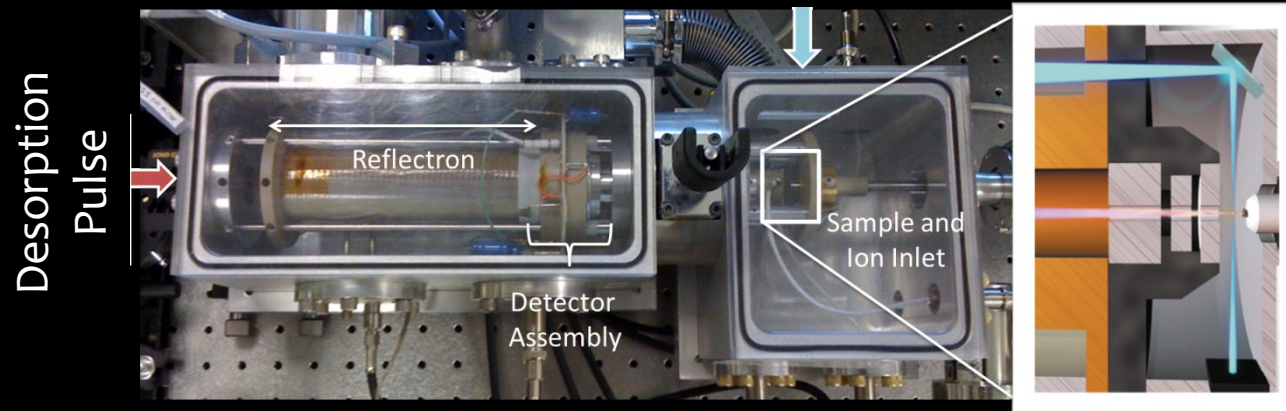
Precision Ion Gating



Fragment Analysis

FEATURES AND OPERATING PRINCIPLES

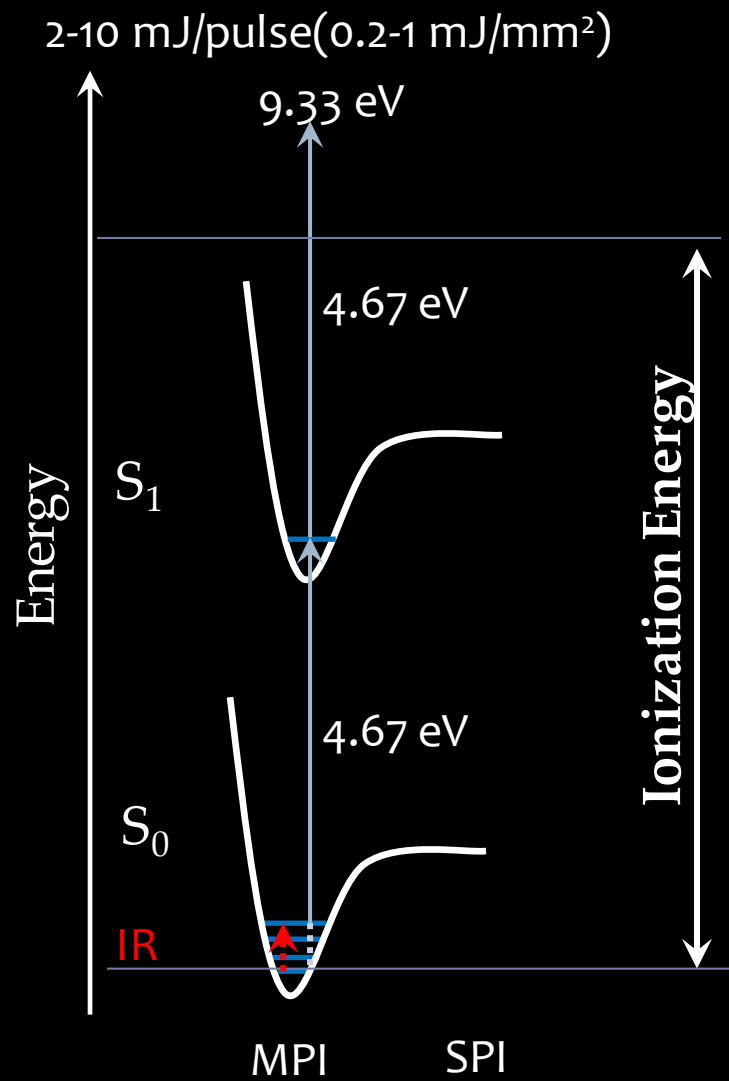
Two-Step Laser MS



Precision Ion Gating



Fragment Analysis



Resonance Enhanced Multiphoton Ionization

Selective ionization:

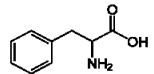
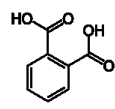
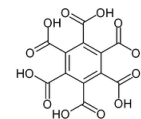
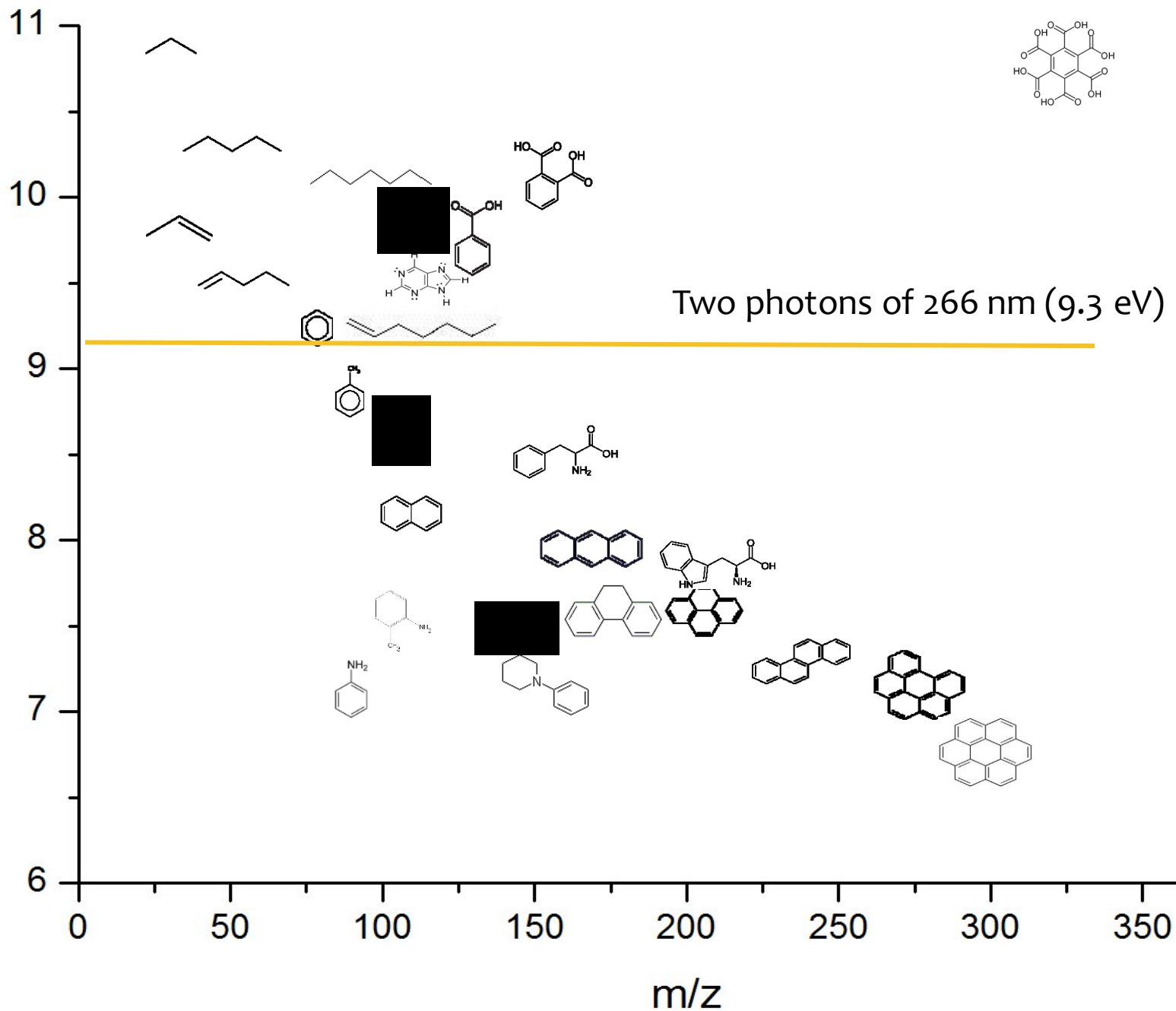
- A. molecules ionization energy is lower than the two-photon energy
- B. intermediate state can be pumped by one-photon absorption

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)

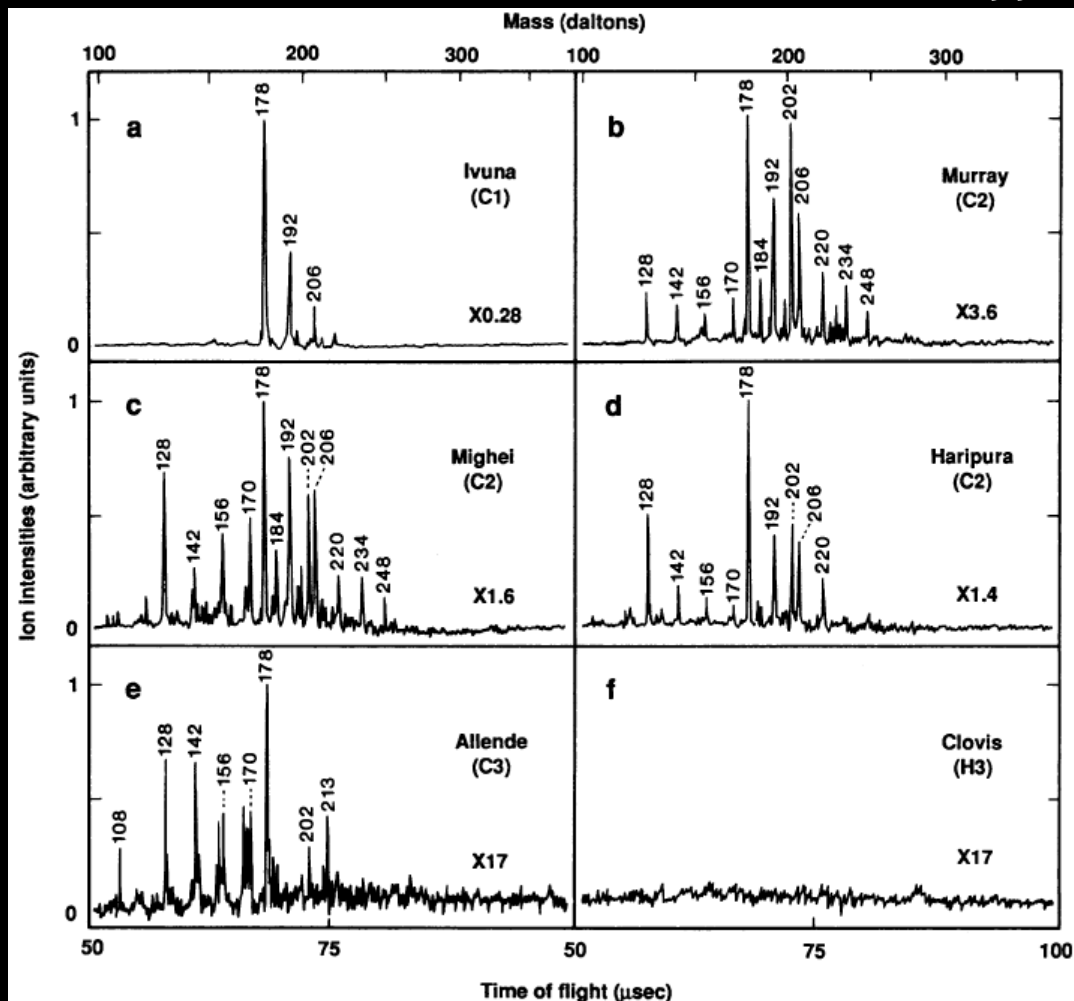


Two photons of 266 nm (9.3 eV)

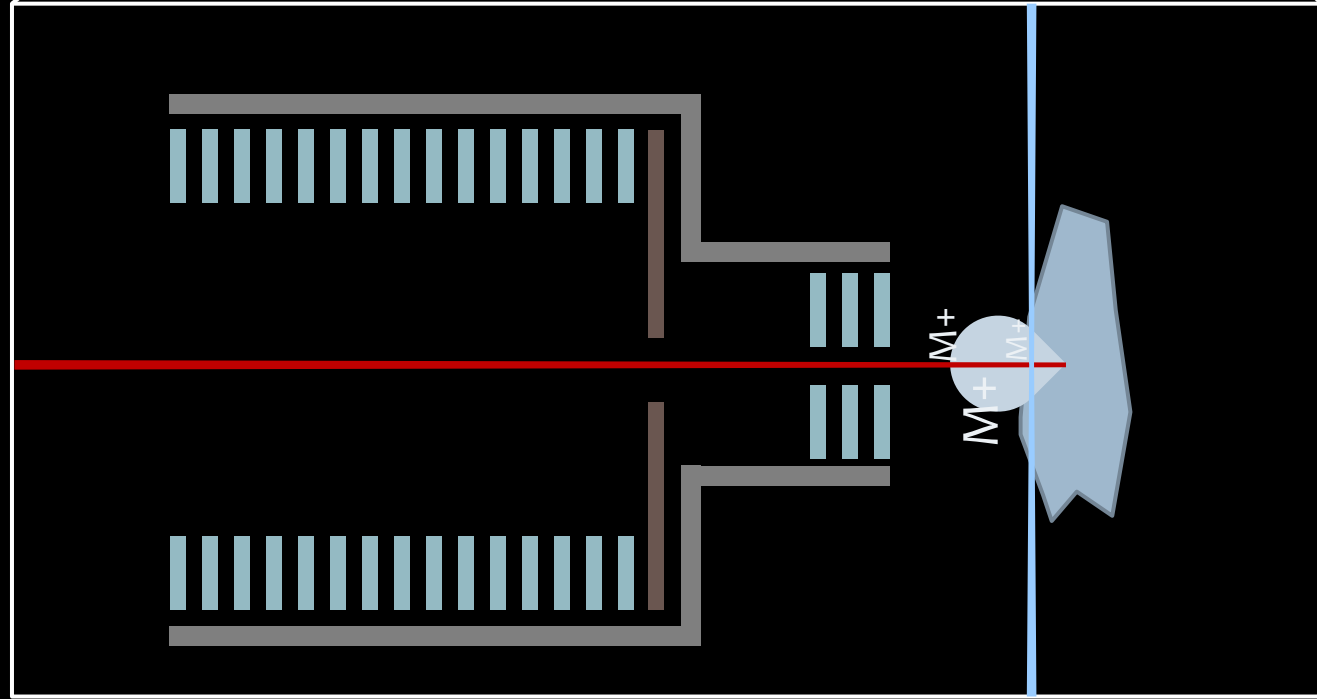
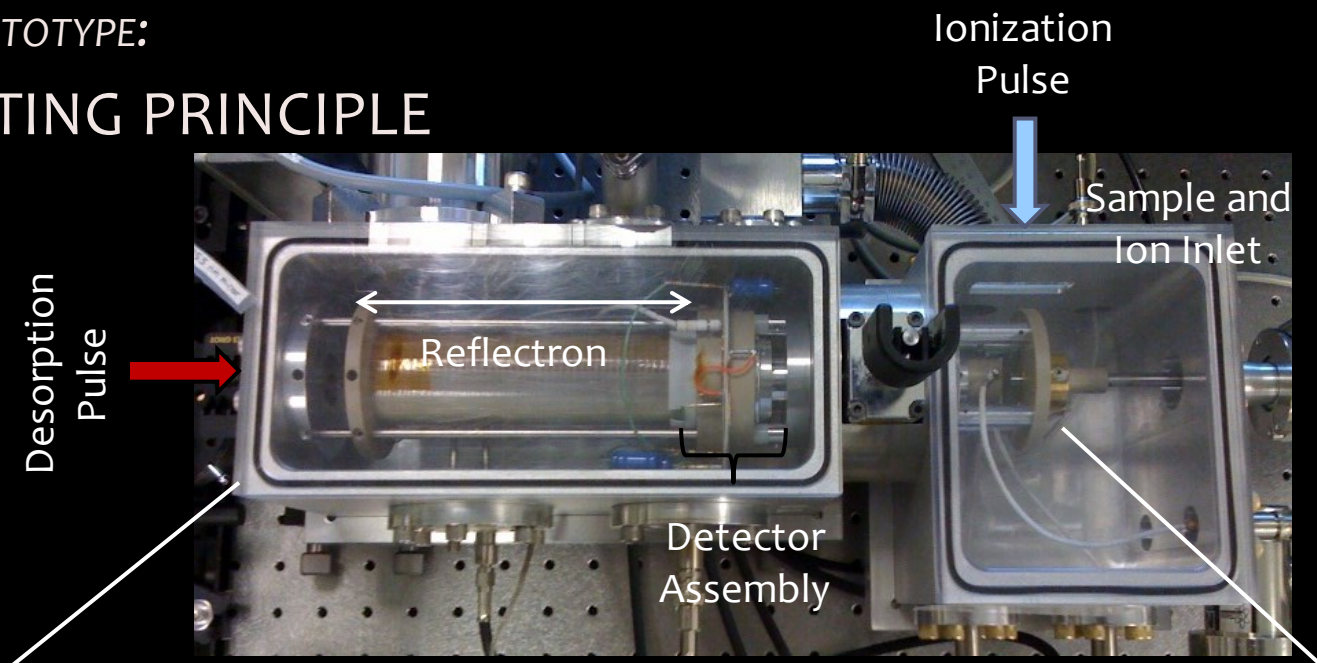
MOLECULAR SPECIFICITY

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:

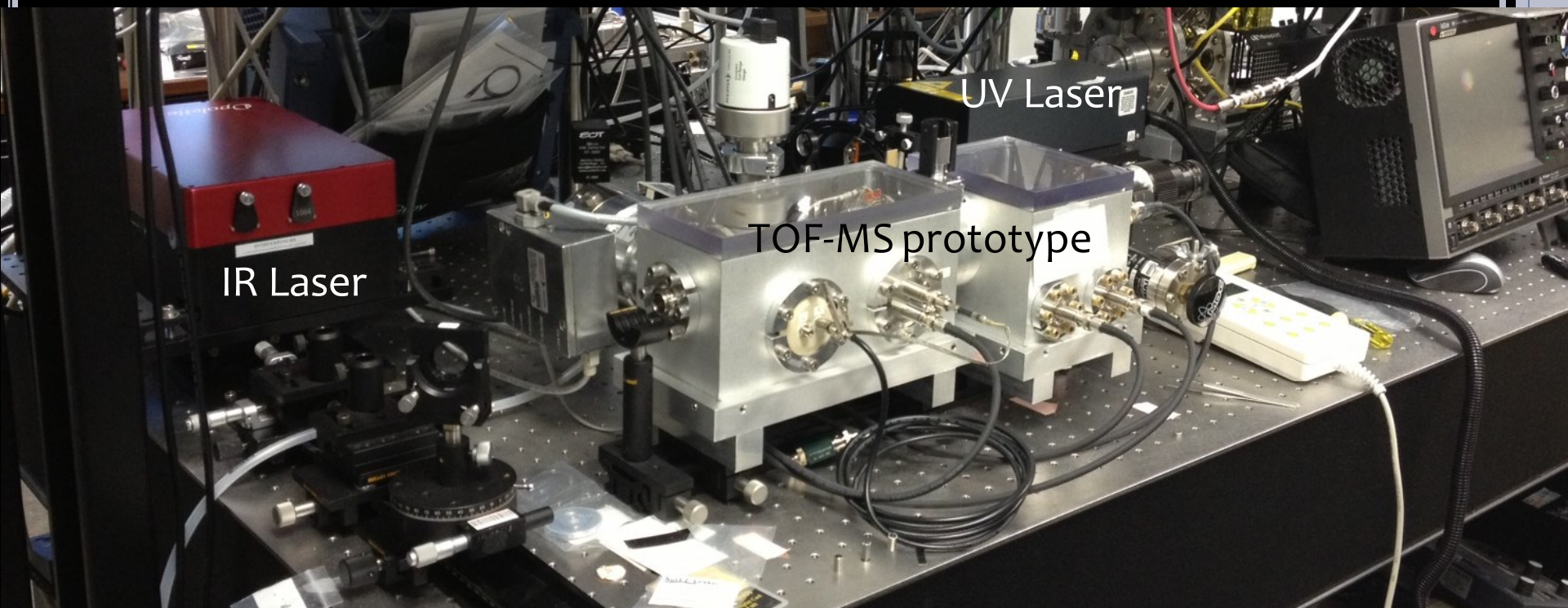
LABORATORY EXPERIMENT

IR Laser:

- 1064 nm Nd:YAG
- 2.7 to 3.1 μm tunable OPO
- 10 μm CO₂

UV Laser:

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

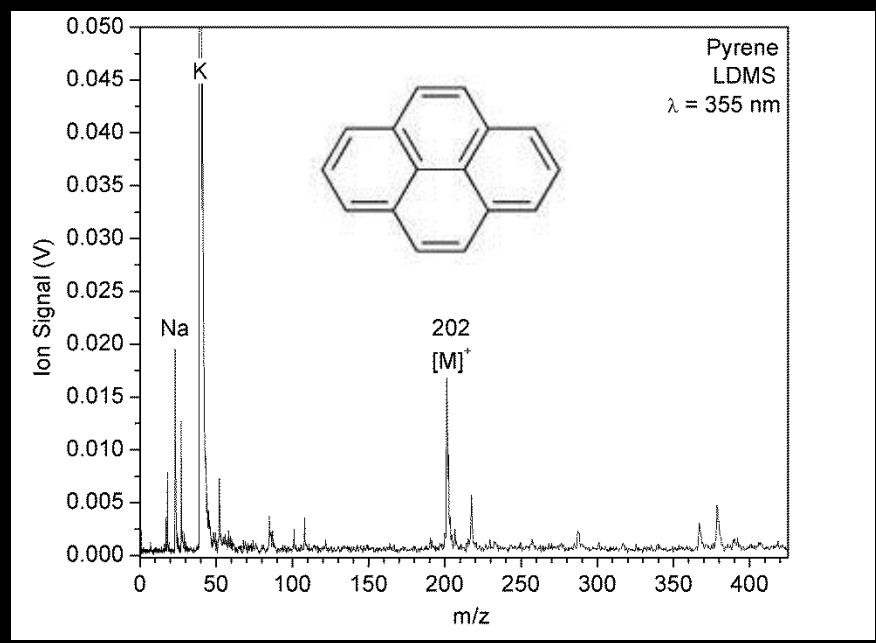


IR Laser

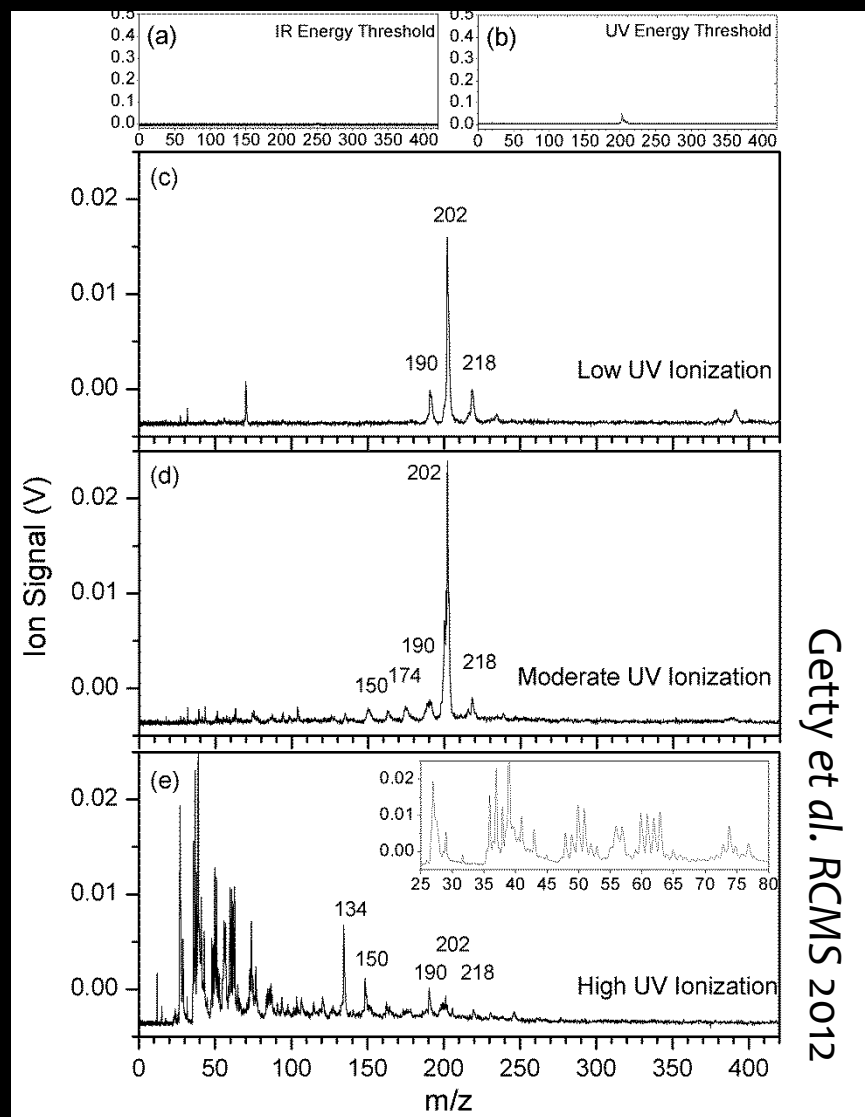
TOF-MS prototype

UV Laser

SELECTIVITY TO AROMATICS

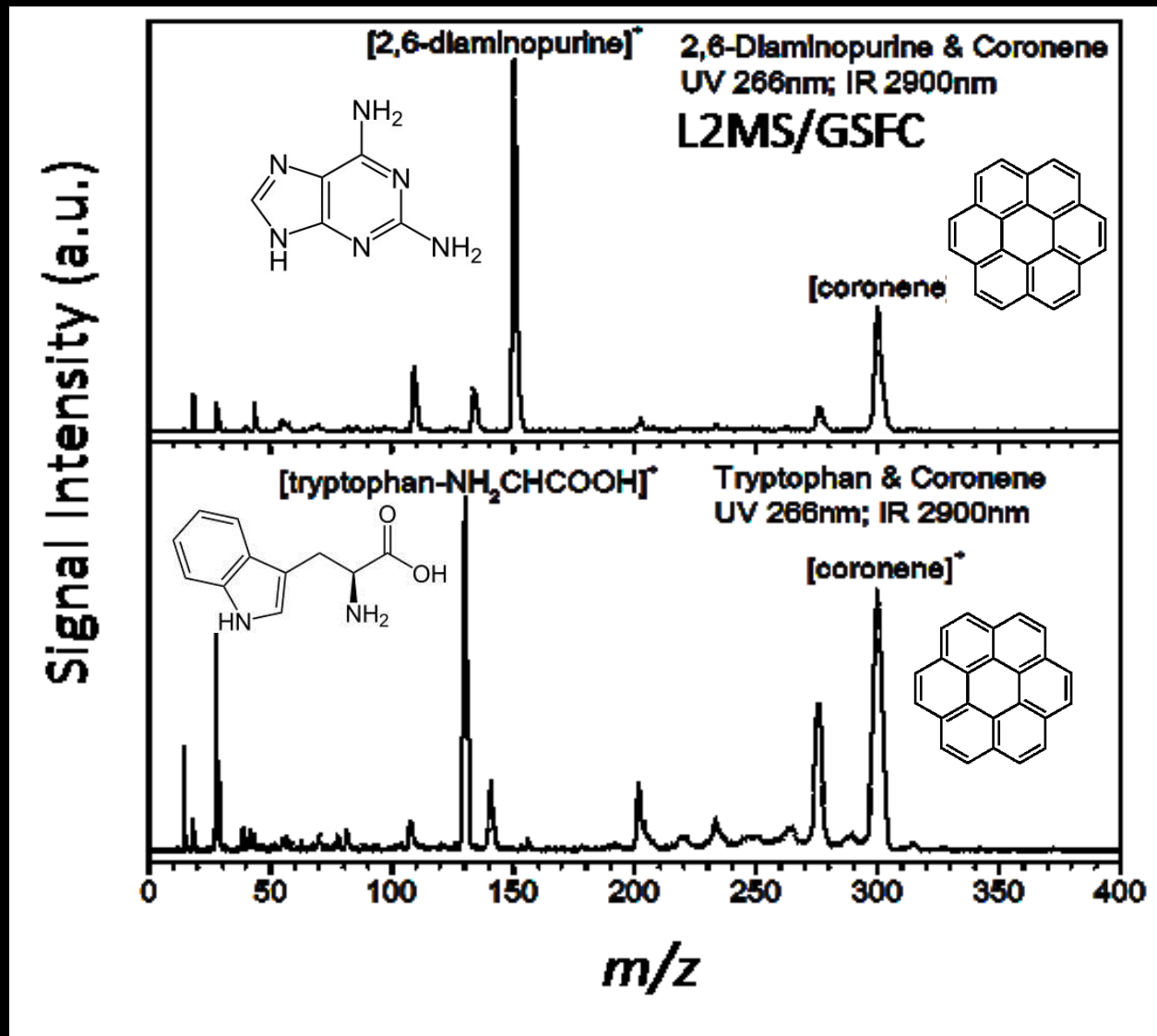


Model aromatic: pyrene
m/z 202



Getty et al. RCMS 2012

SELECTIVITY TO AROMATICS

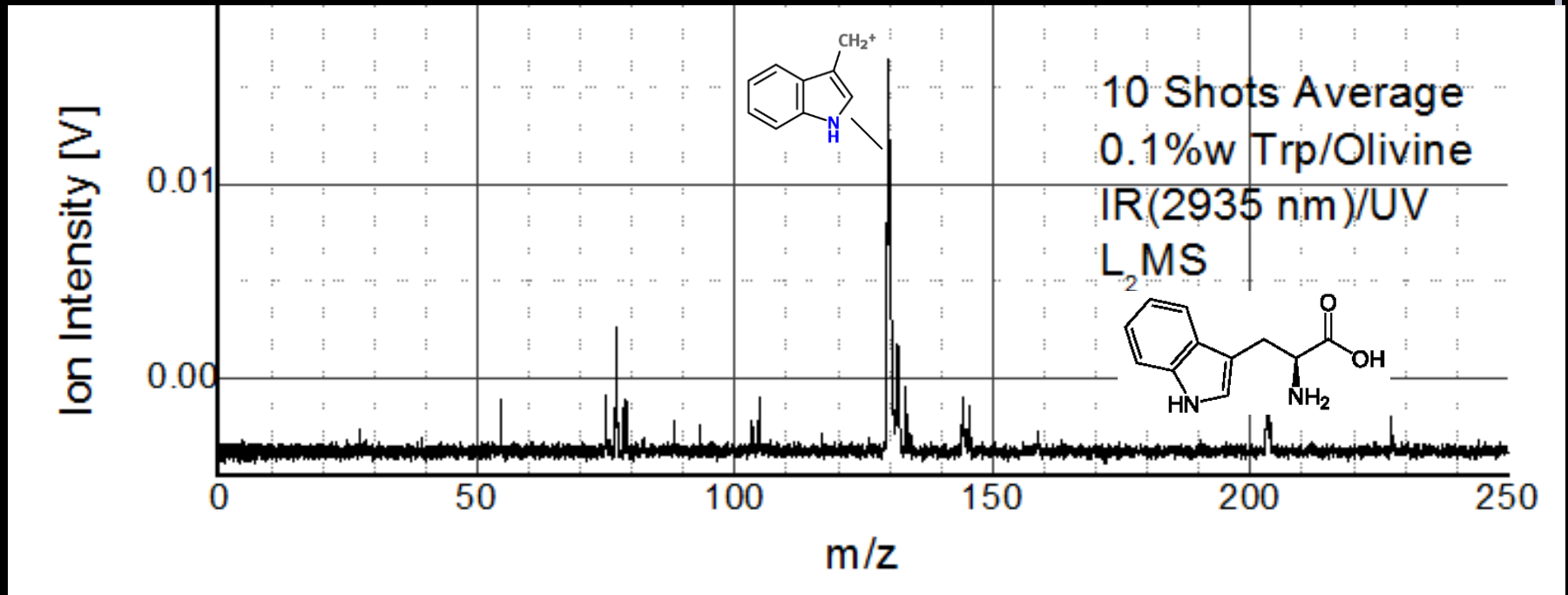


Getty et al. IEEE AeroConf 2014

L₂MS PROTOTYPE:

SENSITIVITY TO PREBIOTIC SPECIES

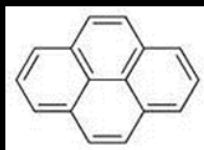
IN THE PRESENCE OF A MINERAL MATRIX



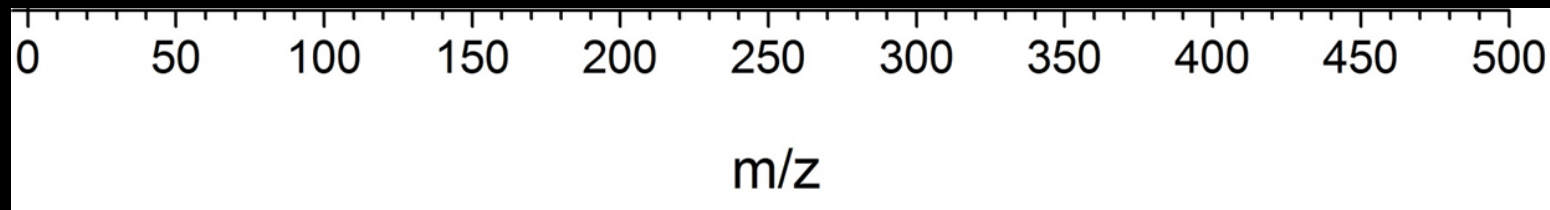
L2MS – SELECTIVITY IN IONIZATION STEP



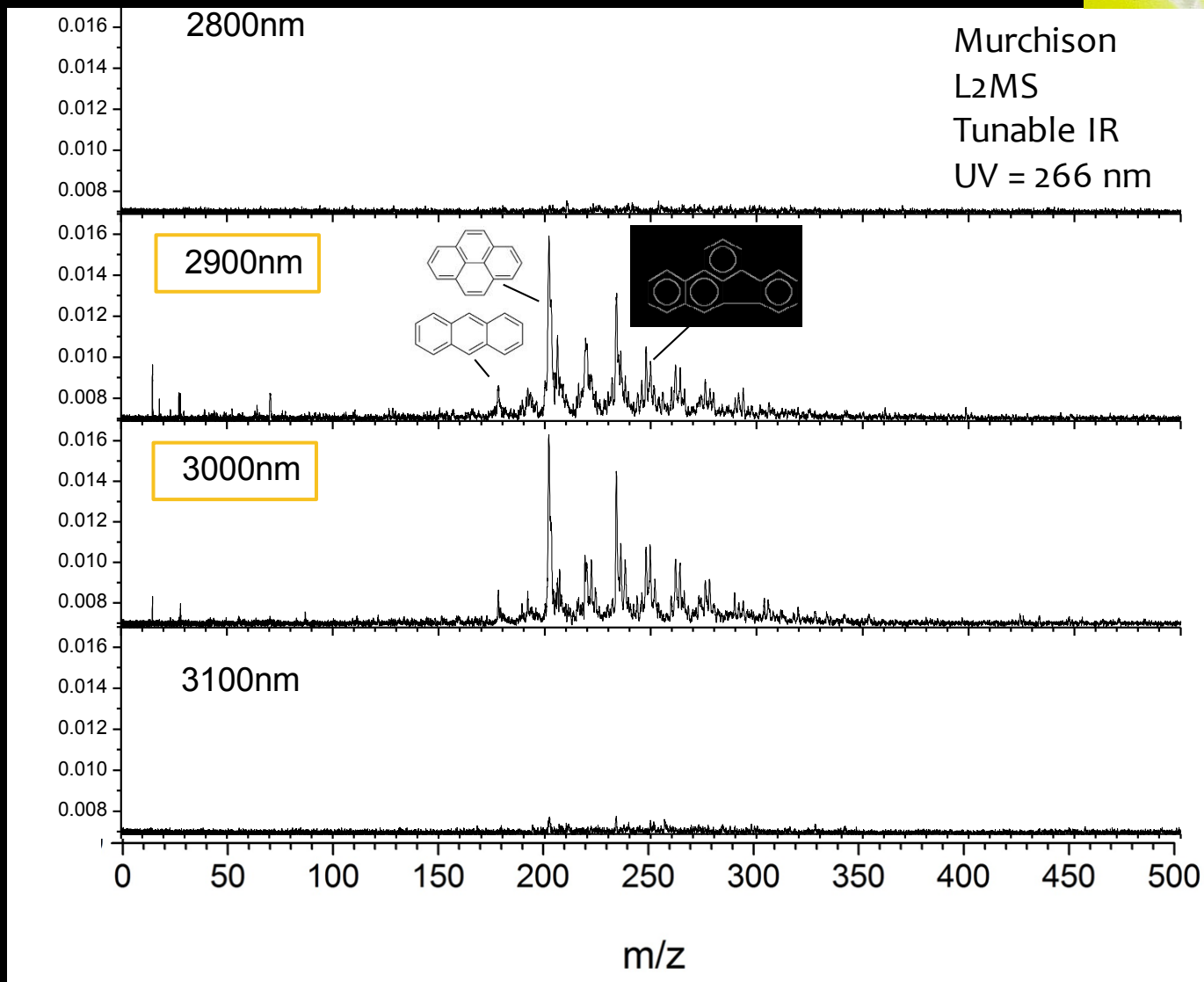
Murchison powder
L1MS mode



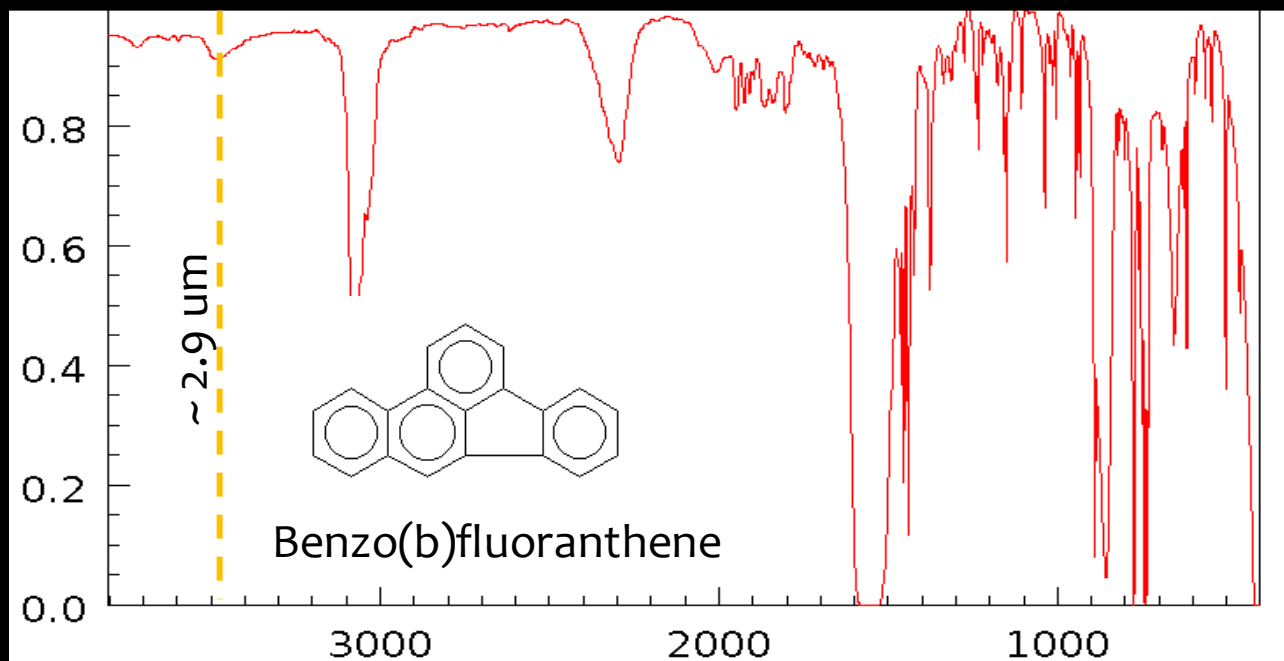
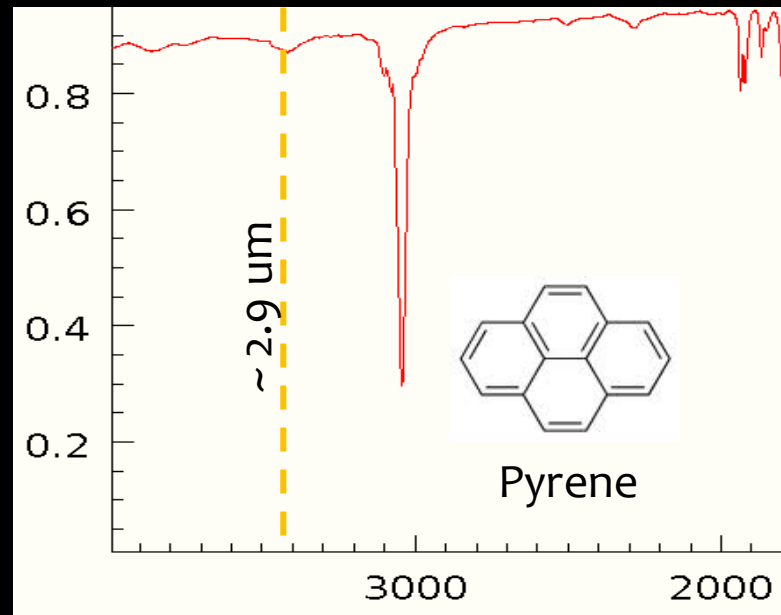
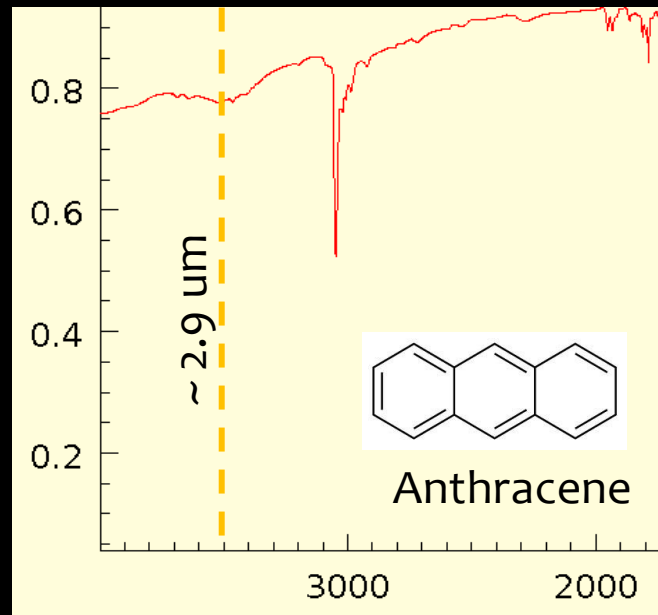
Murchison
L2MS mode



L2MS – SELECTIVITY IN DESORPTION STEP



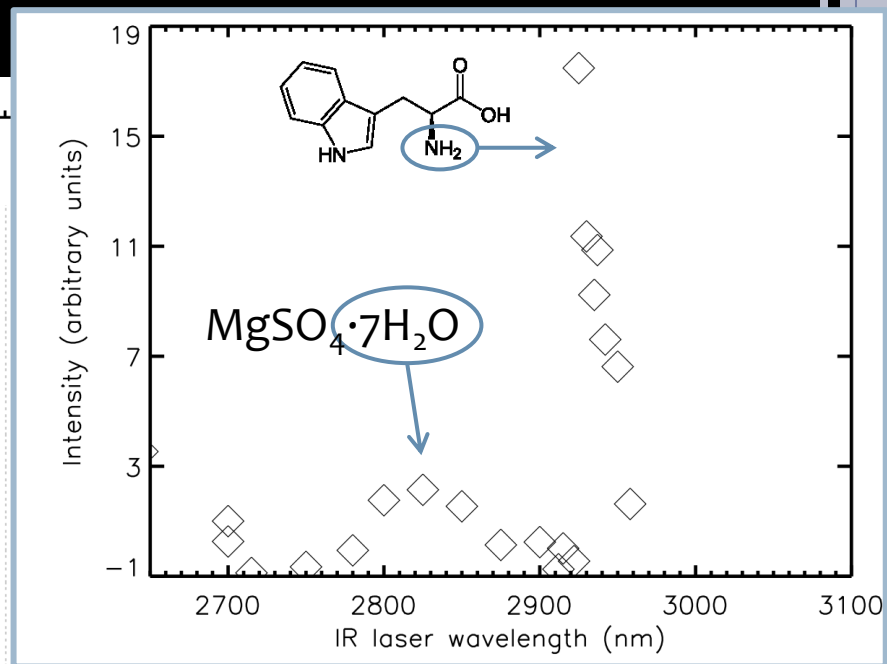
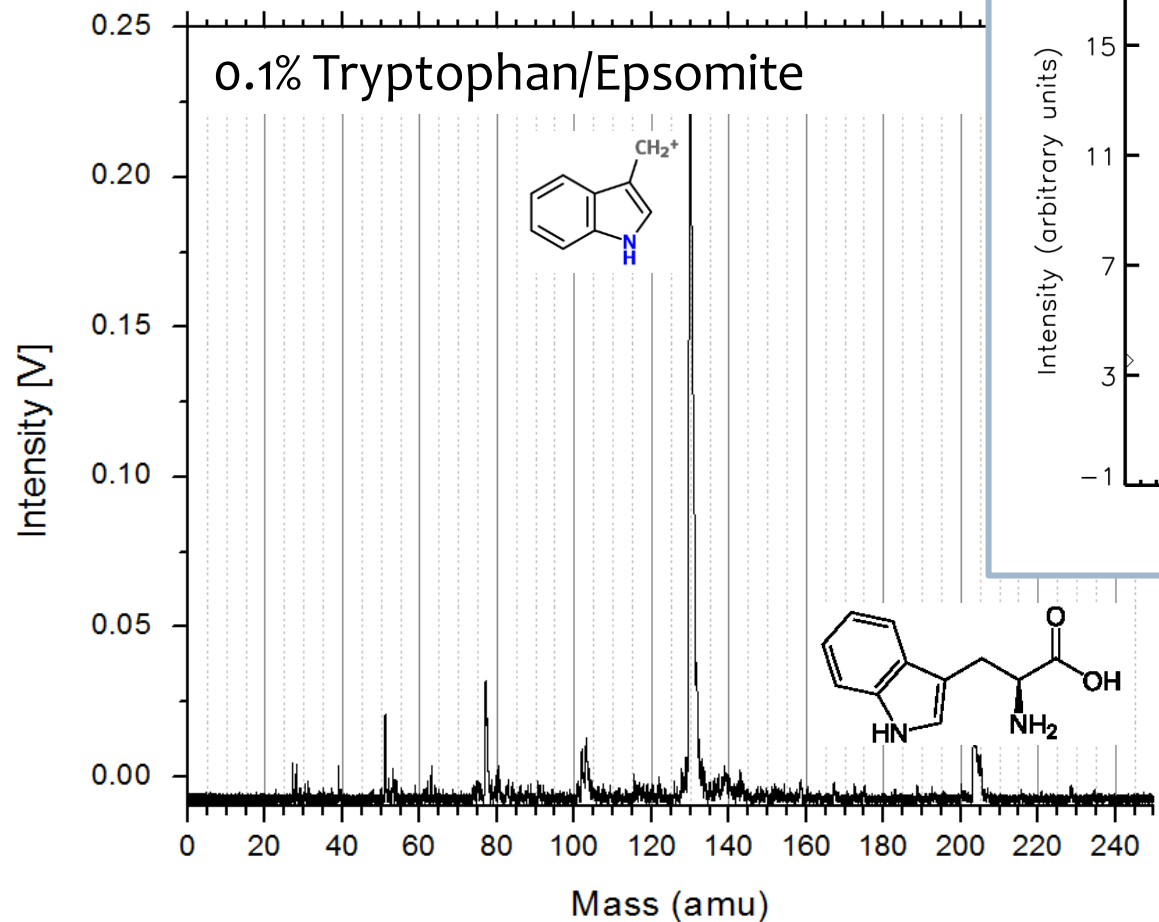
Transmittance



Wavenumbers (cm-1)

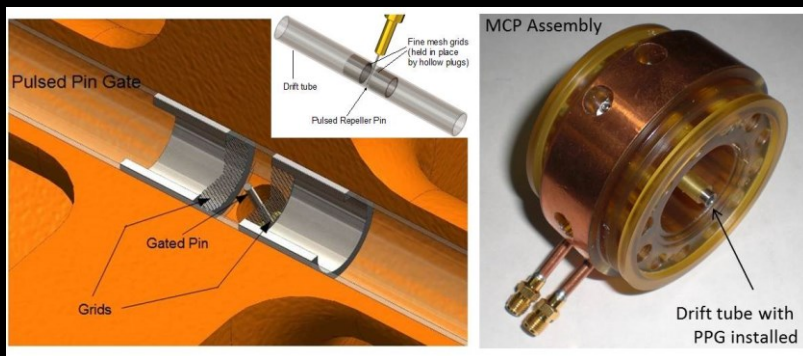
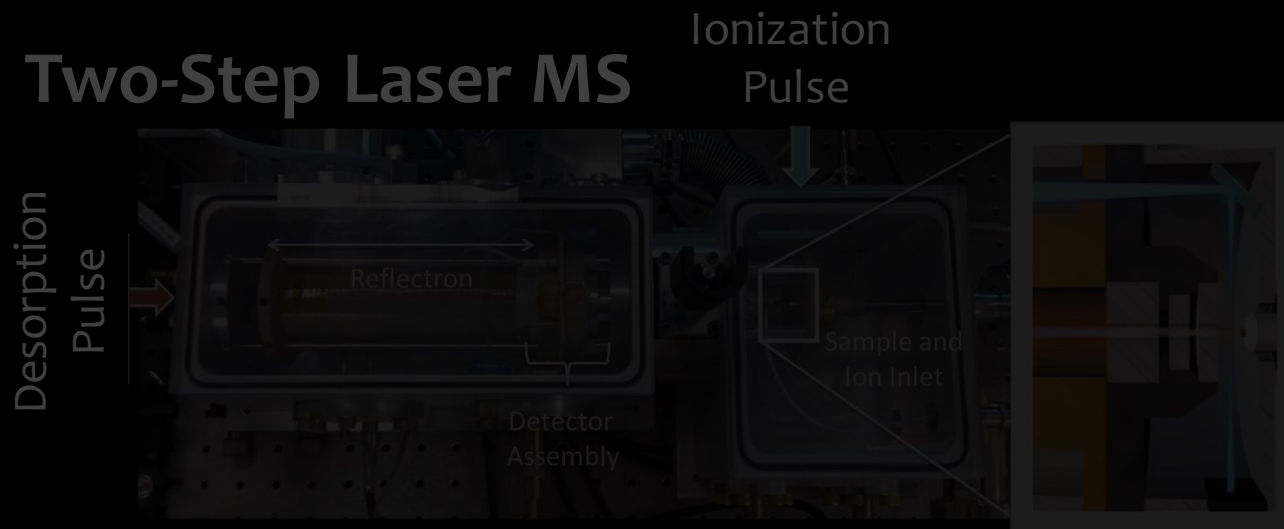
IR TUNABILITY CAN EXPLOIT RESONANCES

FOR HIGH SENSITIVITY



FEATURES AND OPERATING PRINCIPLES

Two-Step Laser MS



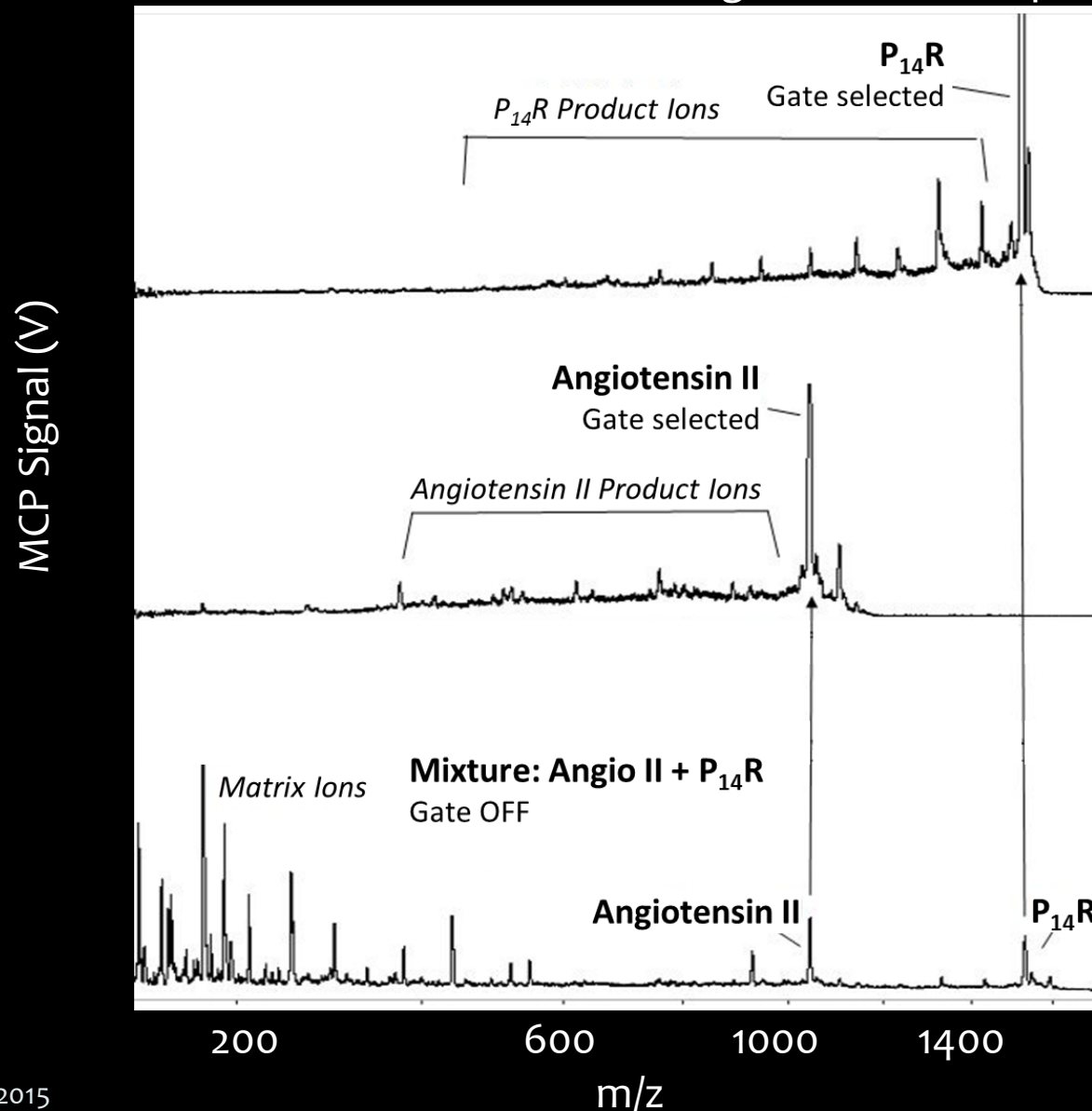
Precision Ion Gating



Fragment Analysis

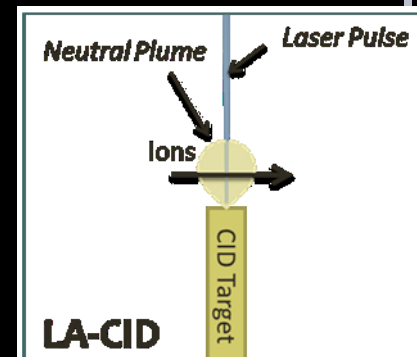
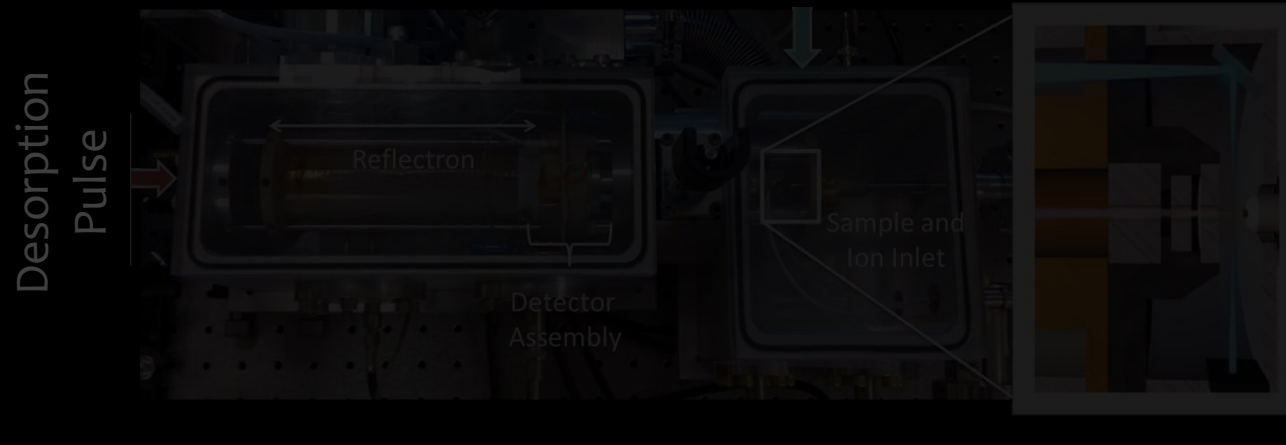
PRECISION ION GATING AND TANDEM MS

Structural determination using MS/MS techniques

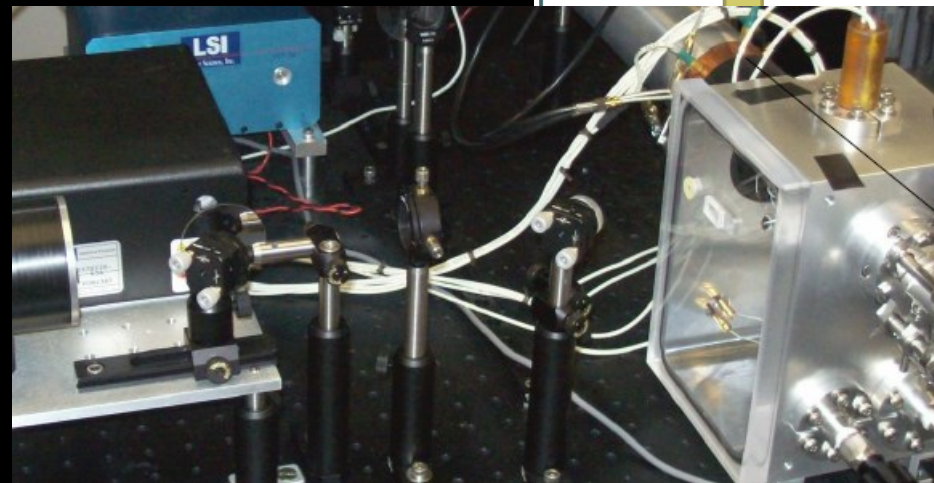


FEATURES AND OPERATING PRINCIPLES

Two-Step Laser MS



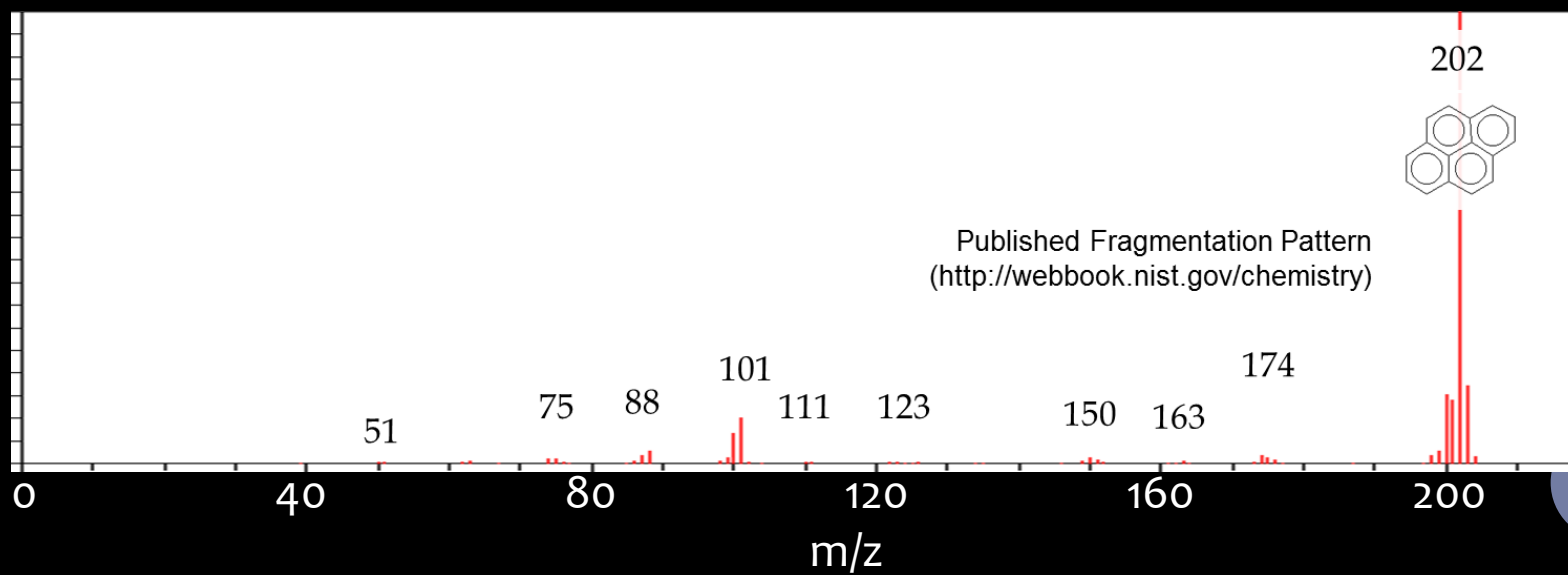
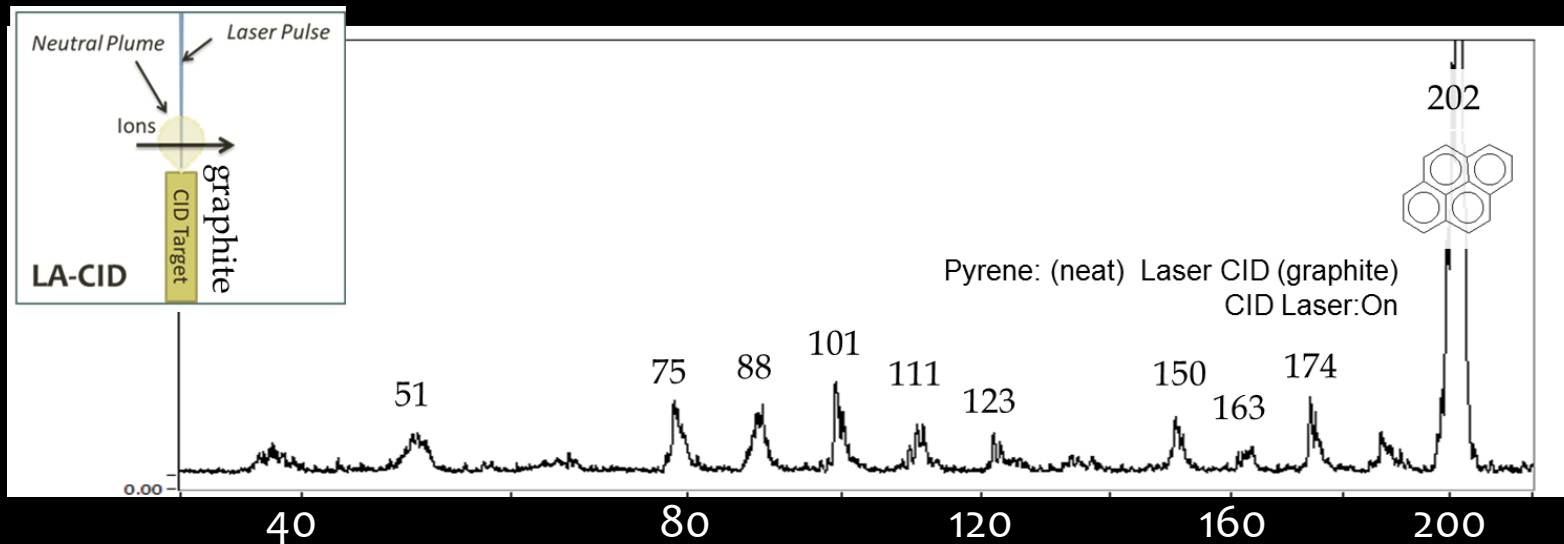
Precision Ion Gating



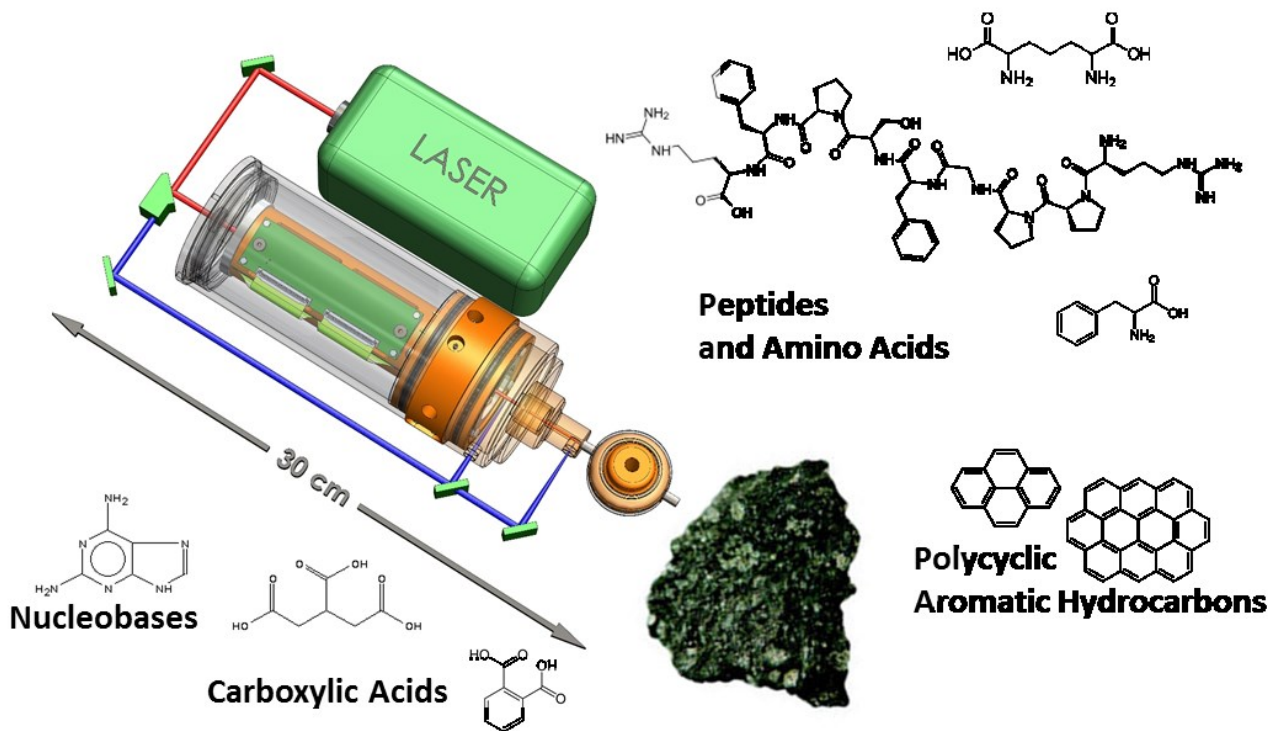
Fragment Analysis

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

