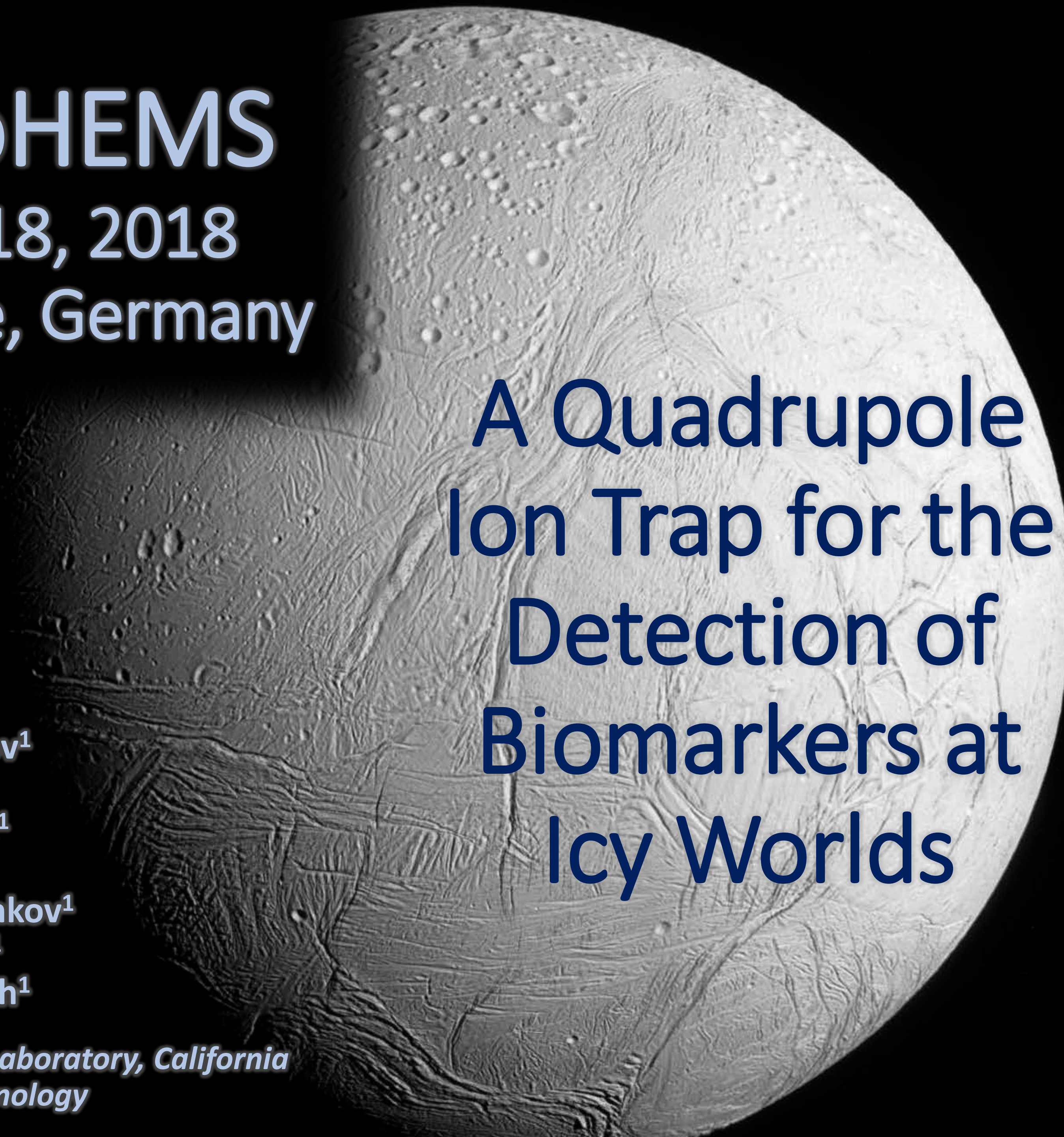
EuroHEMS
Oct. 18, 2018
Cologne, Germany



A Quadrupole Ion Trap for the Detection of Biomarkers at Icy Worlds

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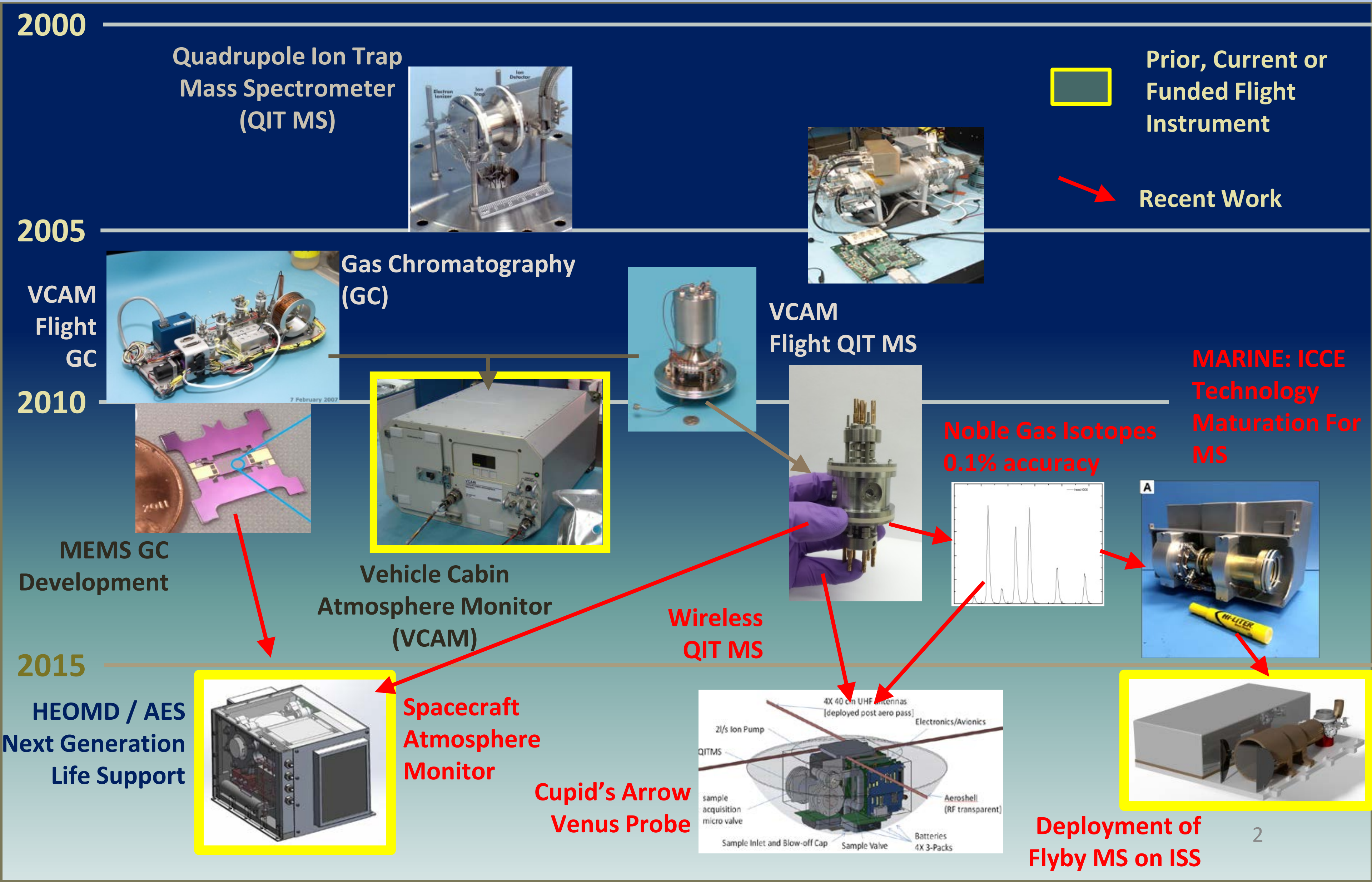
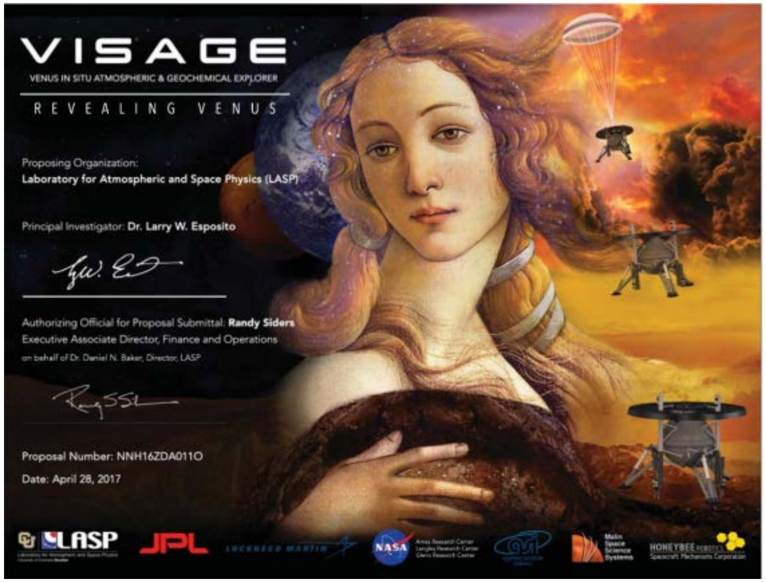
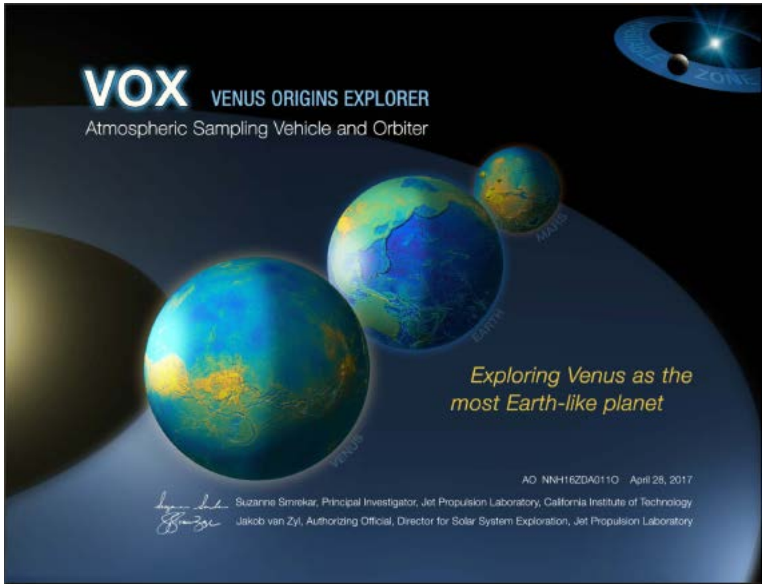
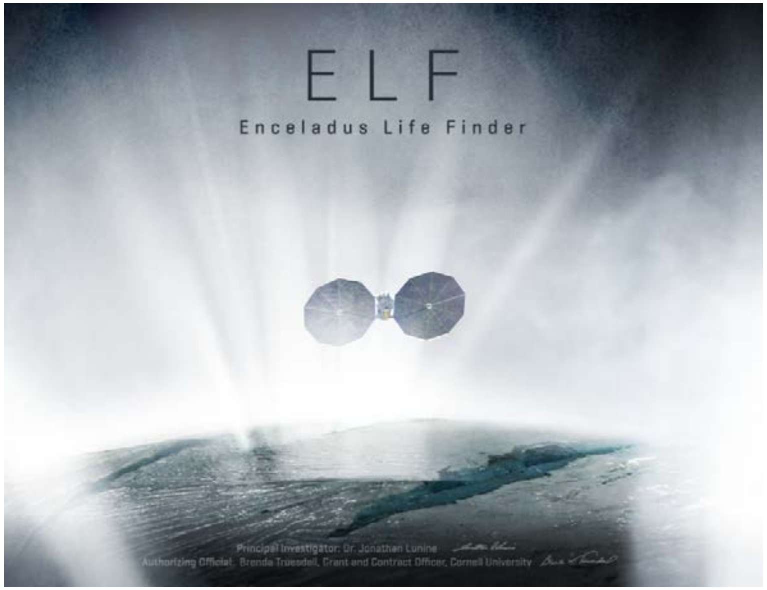
QIT-MS Development at JPL

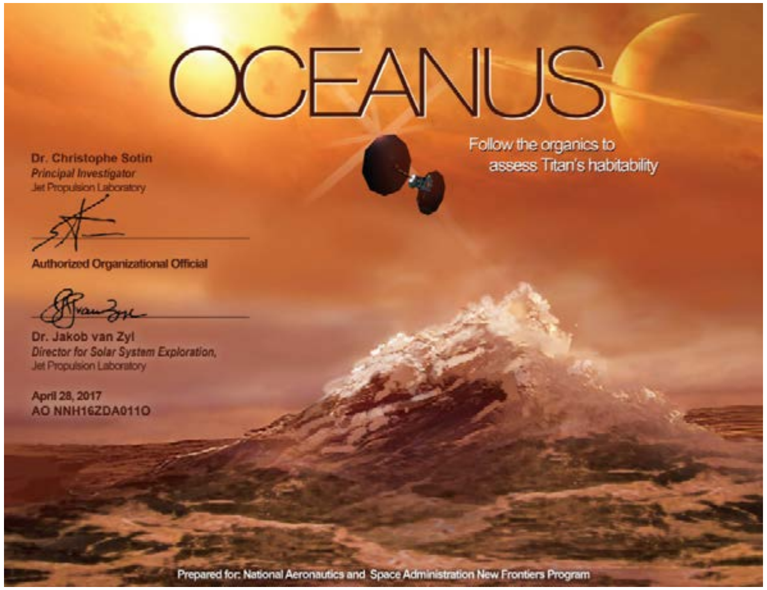


QIT-MS on 4 New Frontiers Concepts





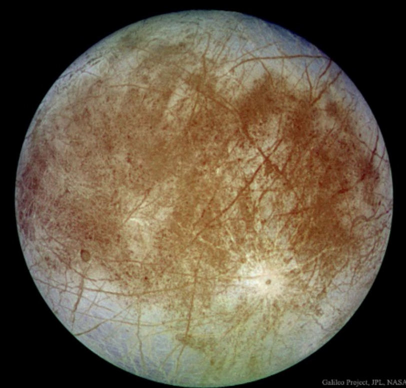




Search for Life: Icy Worlds

- Ingredients for life (as we know it):
  - Water
  - Organic carbon
  - Energy source
  - Other elements: N, S, P
- 5 icy moons in our solar system that could potentially host life
- Need instruments for lander and orbiter missions to search for signs of life (e.g. fatty/amino acids)

Jupiter

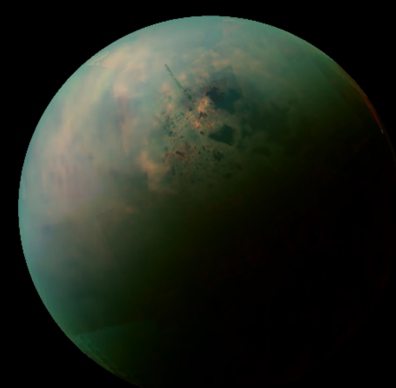


Europa

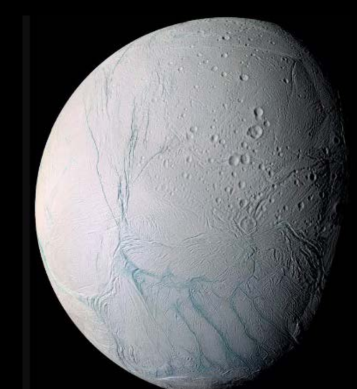
Callisto

Ganymede

Saturn



Titan

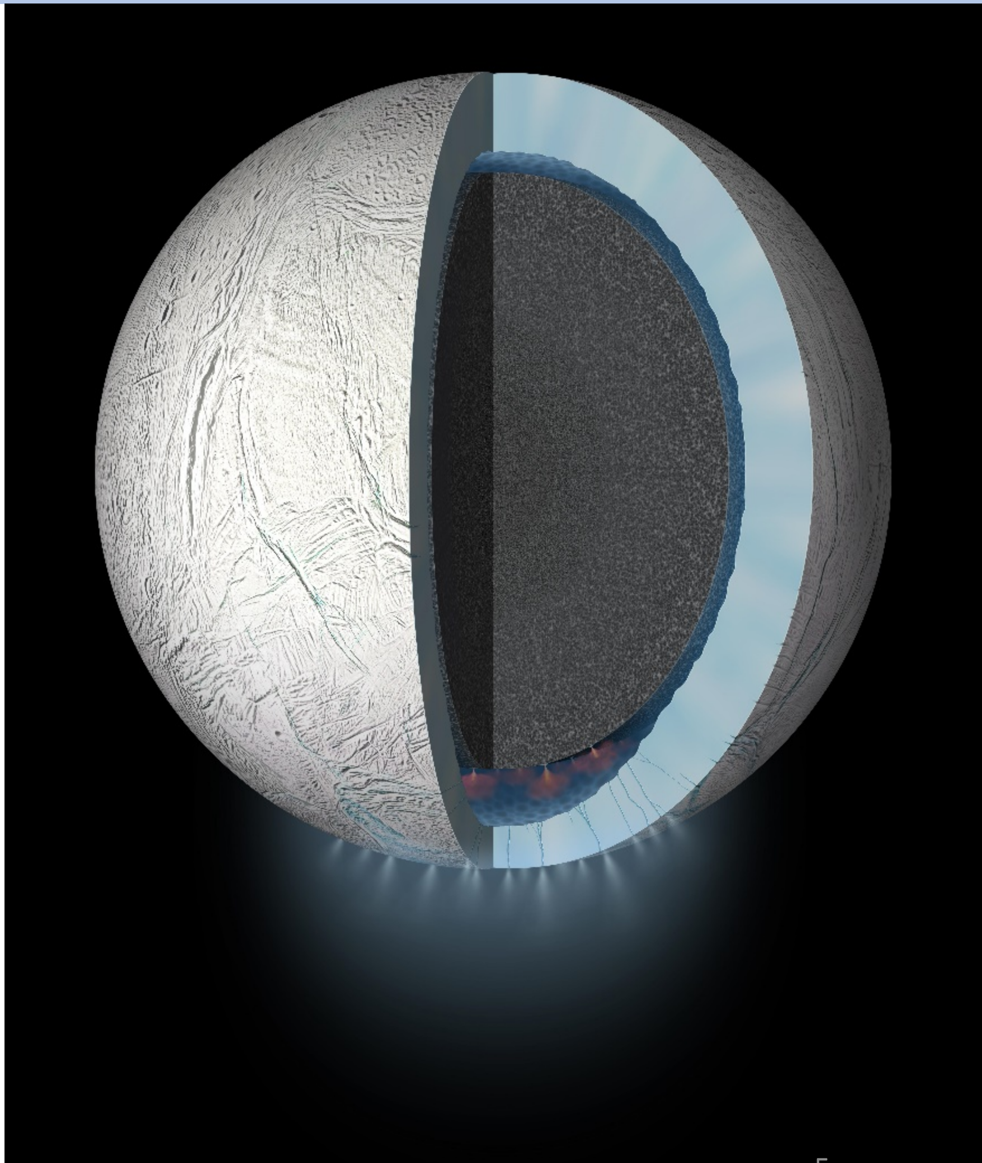


Enceladus

Images: NASA

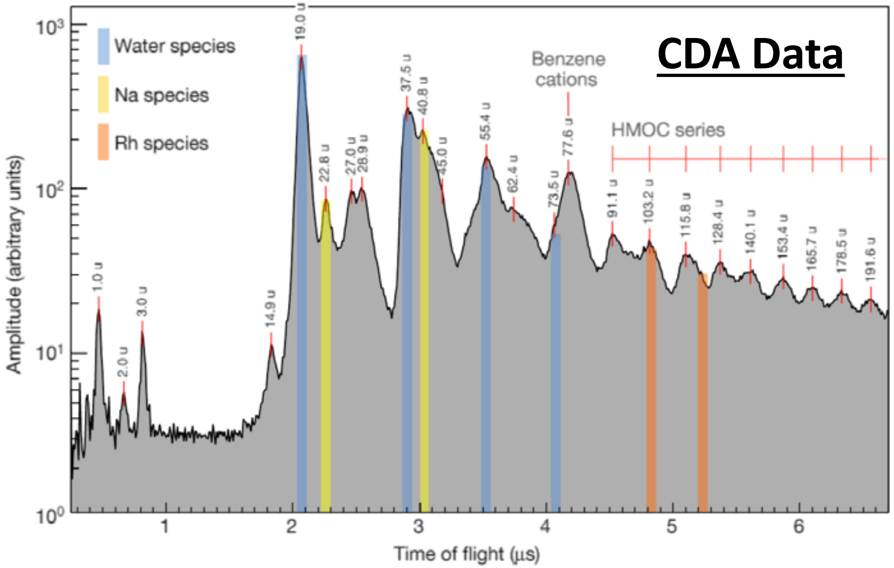
Enceladus

- Discovered by William Herschel in 1789 (named by son John in 1847)
- 500 km diameter
- Cryovolcanoes on the south pole eject ice, water vapor, H_2, NaCl, etc.
    - ~200 kg of material per second
    - ~500 km from the surface
- Widely accepted to have a large, salty, and subsurface ocean
- Over 100 geysers identified
- Ice particles make up Saturn’s E-Ring

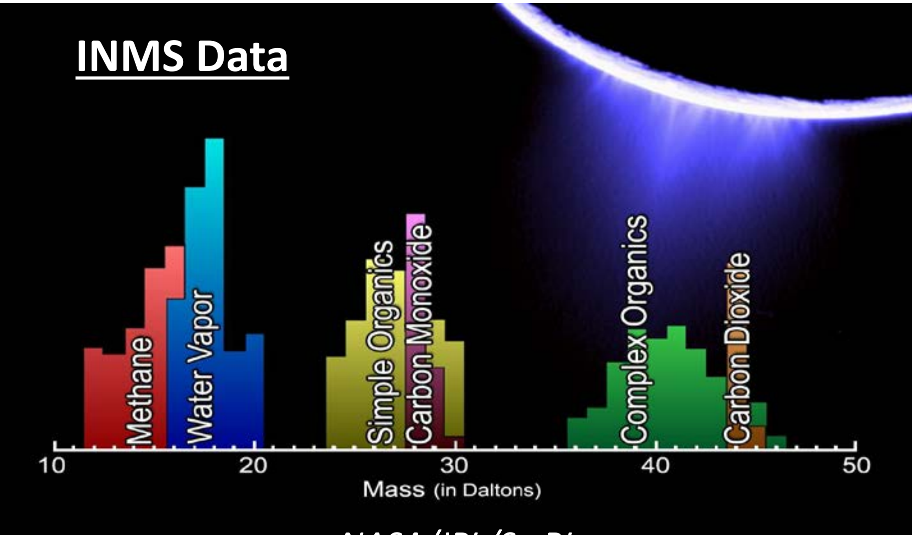


NASA/JPL-Caltech

Cassini: Enceladus' Ice Grain Analysis



Postberg, F.; *et al. Nature*, 558, p. 564, **2018**



NASA/JPL/SwRI

Two mass analyzers were aboard Cassini

- Cosmic dust analyzer (CDA)
- Ion and Neutral Mass Spectrometer (INMS)

CDA:

- Time-of-Flight mass spectra of cations generated by high velocity (4-18 km/s) impacts of ice/dust grains on Rhodium target
- Mass range 1 – 200 Da (up to 8,000 Da)
- Mass resolution (m/Δm): 20-50

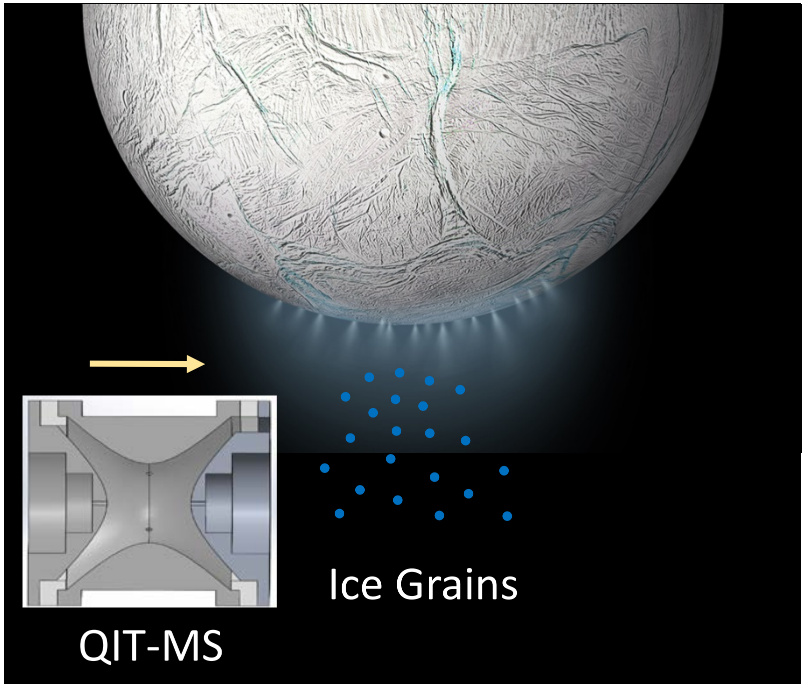
INMS:

- Detects ions and neutrals with quadrupole mass filter
- Mass range: 1 – 99 Da

Together, the CDA and INMS detected, water, salts (NaCl), benzene, methane, carbon dioxide and complex organics

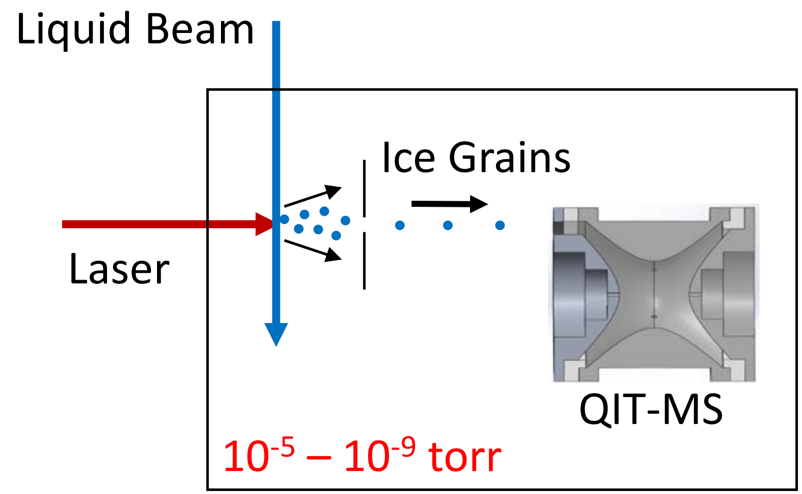
Sampling Hypervelocity Ice with QIT-MS

Ice Grain Sampling at Enceladus



- QIT-MS aboard spacecraft travelling several km/s
- Ice grains from Enceladus' ocean are sampled by QIT-MS

Ice Grain Sampling in the Lab



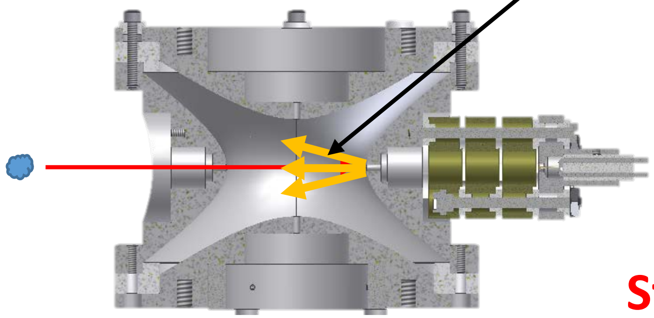
- Liquid beam formed in vacuum
- Laser impinges on liquid beam and causes shock wave-induced anisotropic dispersion of small droplets
- Small droplets travel at a few km/s into QIT-MS

Goal: Mimic ice grain size and relative velocity in the lab

Internal Ionization of Neutral Species Produced by Ice Grain Volatilization

Step 1

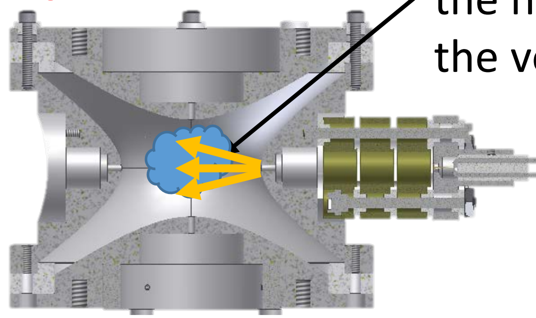
Ionizing e^- beam in the QITMS



Ice grain at 5-7 km/sec enters QITMS and strikes surface causing volitization

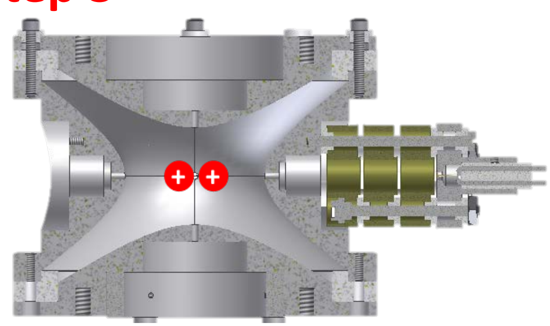
Step 2

e^- beam or chemical ionization of the neutral gas molecules from the volatilized ice grain form ions



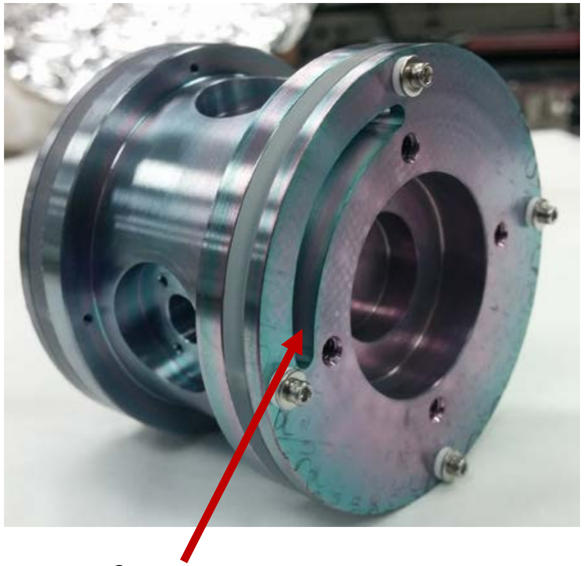
Step 3

Ions are mass analyzed by multi-stage mass spectrometry



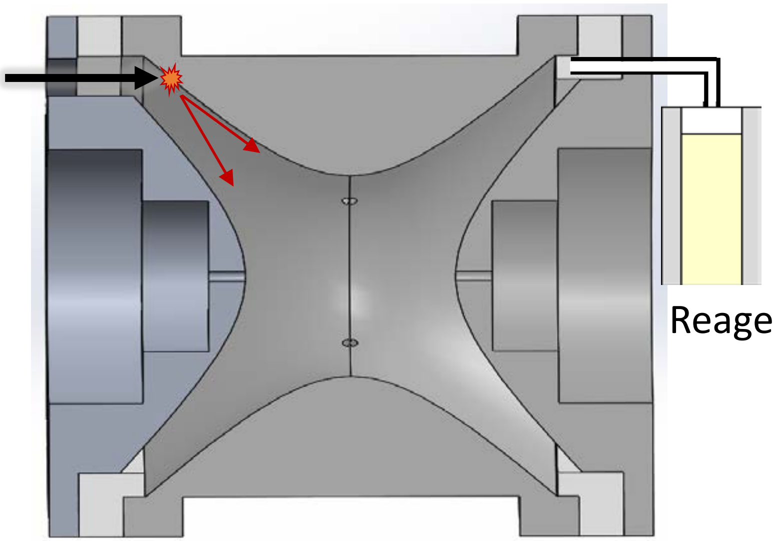
Modifications to QIT-MS for Low Vapor Pressure Molecule Analysis

Photo of Modified QIT-MS



1 cm^2 slot for ice grains

Solution Injection in QIT-MS Diagram



EI – Low Pressure of R (<10^{-5} torr):
CI – High Pressure of R (>10^{-5} torr):

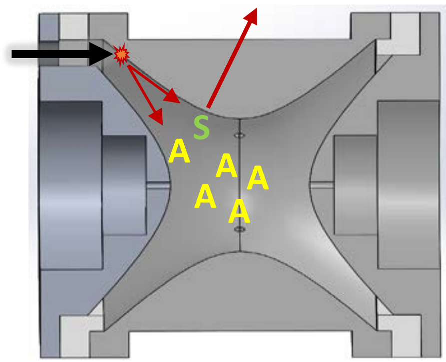
- Slot cut into QIT end cap to accept ice grains
- Trap coated with silicon-based SilcoTek coating to prevent analyte "sticking"
- Fatty/Amino solutions pumped directly into QIT-MS slot (QIT temperature: 125 ˚C)
- Adding a "reagent" allows chemical ionization (CI)
- Absence of a "reagent" results in electron ionization (EI)

Various Ionization Modes

Electron Impact

- Solvent and analyte pumped into QIT
- After some time, solvent is pumped away but analyte remains
- Electron beam ionizes analyte

Solvent (S) +
Analyte (A)



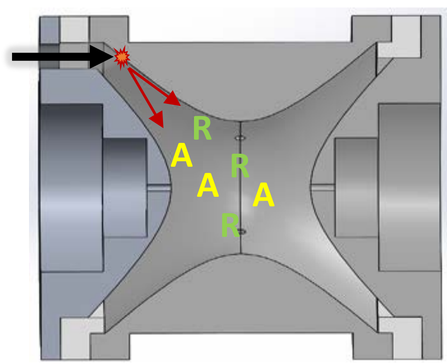
$$e^- + A \longrightarrow A^+ + 2e^-$$

Chemical Ionization

Method 1:

- Solvent and analyte continuously pumped into QIT
- Solvent is used as reagent for CI

Solution:
Reagent (R) +
Analyte (A)

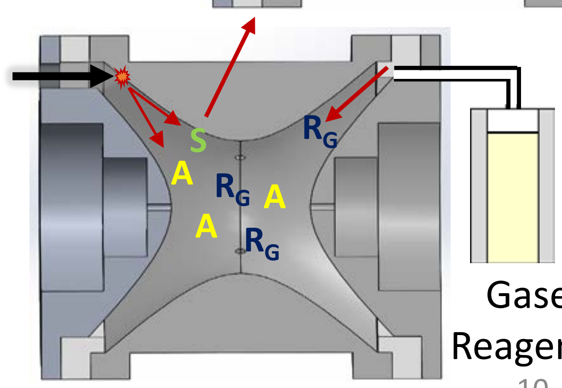


$$RH^+ + A \longrightarrow AH^+ + R$$

Method 2:

- Solvent and analyte pumped into QIT
- After some time, solvent is pumped away but analyte remains
- Reagent gas for CI added in separate port

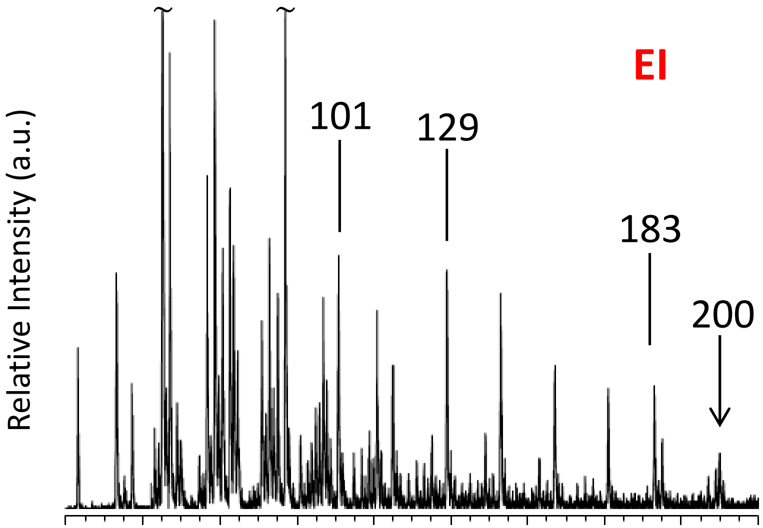
Solution:
Solvent (S) +
Analyte (A)

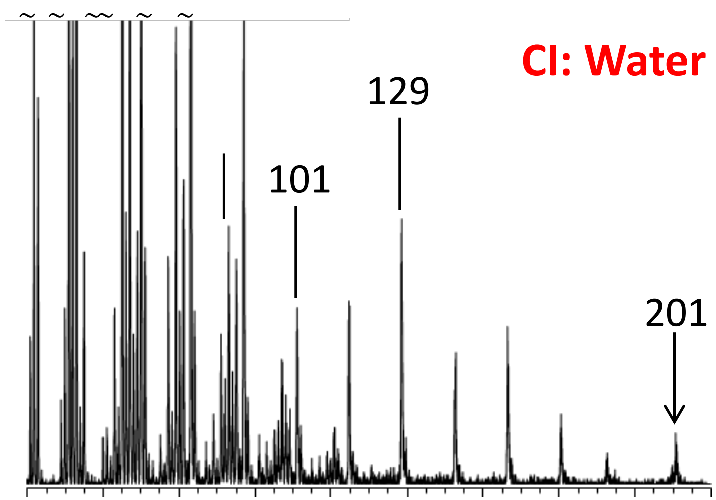


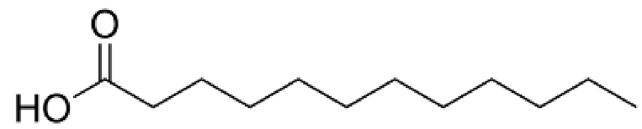
Gaseous
Reagent (R_G)

$$R_GH^+ + A \longrightarrow AH^+ + R_G$$

EI vs. CI







Lauric Acid
MW: 200 amu

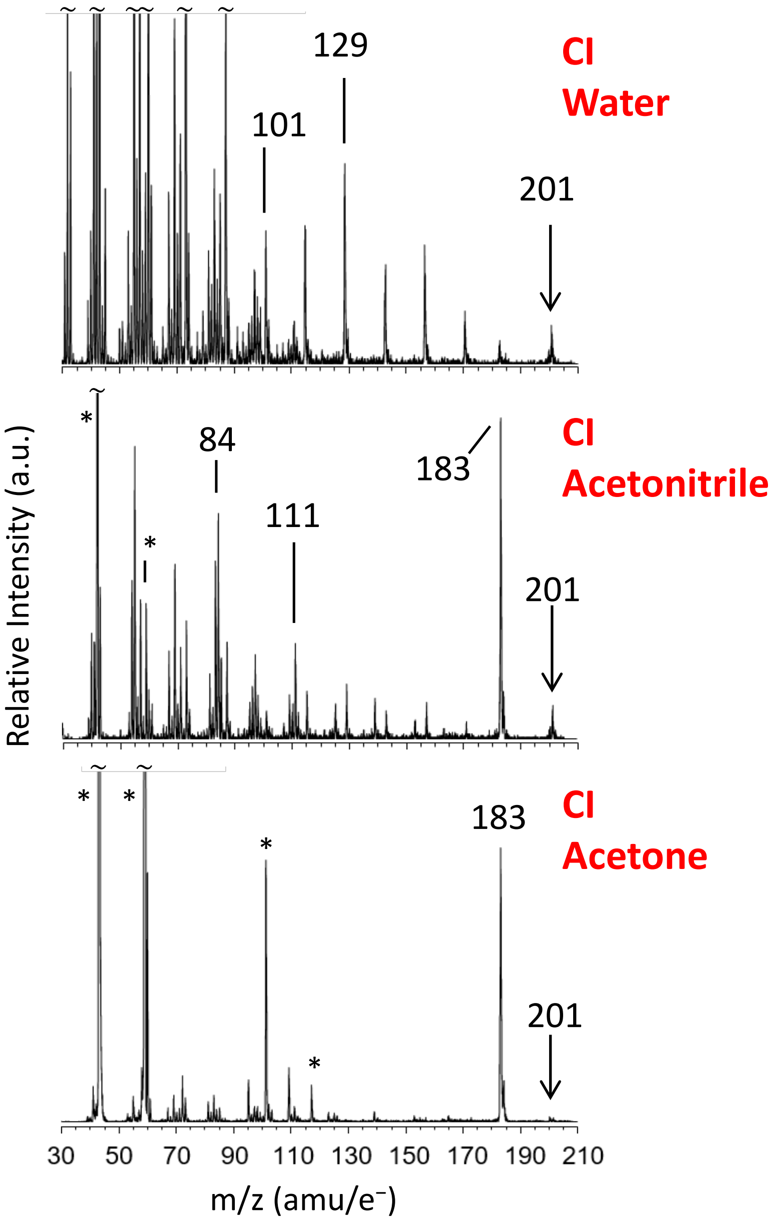
EI

- Causes significant fragmentation ("hard")
  - Complicates mass spectra of mixtures
  - Excellent fingerprint for pure samples
- Parent peak: **Molecular cation**

CI

- Can be "soft" or "hard" depending on reagents/samples
- CI of lauric acid with water is "hard"
  - Similar to EI spectrum
- Parent peak: **Protonated**

“Softening” Chemical Ionization



- <u>Difference in proton affinity</u> determines extent of fragmentation

  Water > Acetonitrile > Acetone

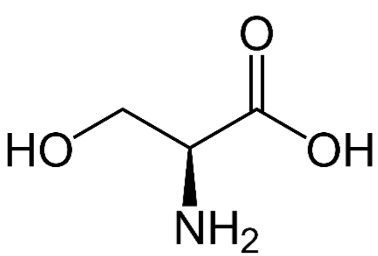
Molecule	PA (kJ/mol)	ΔPA (kJ/mol)
Lauric acid	815-825?	
Water	691	124 (1.3 eV)*
Acetonitrile	779.2	36 (0.4 eV)*
Acetone	812	3 (0.03 eV)*

** Estimated values*

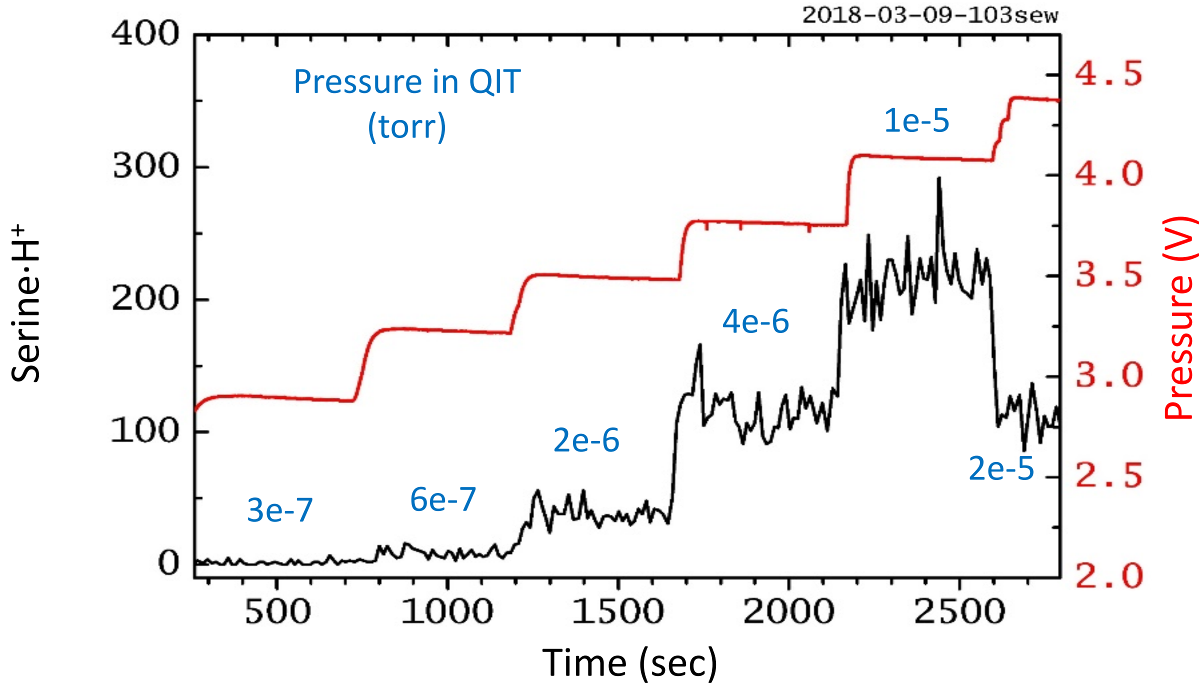
- Mass spectra show less fragmentation as you work down from water to acetone

- Water CI shows more of the protonated parent ion than acetone
  - Likely due to reagent size
  - Should be able to further decrease fragmentation by using a reagent with a similar proton affinity as acetone but lower mass

Pressure Dependence of CI

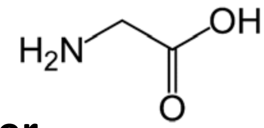


Serine
MW: 105 Da



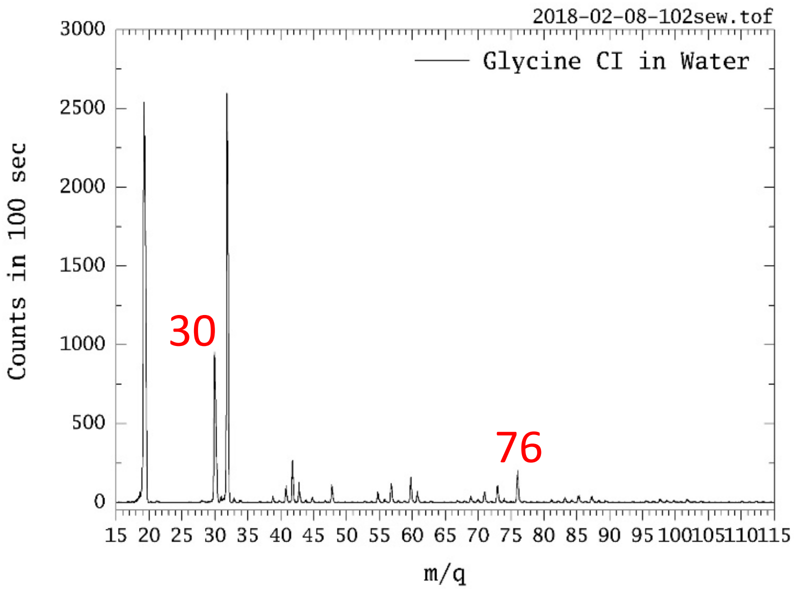
- CI is very sensitive to pressure
- Optimum CI with $1x10^{-5}$ torr acetone in QIT
- Sharp decrease in counts likely due to ion loss from collisions with acetone
  - A lighter CI reagent could possibly reduce signal loss

CI in Water Mixtures

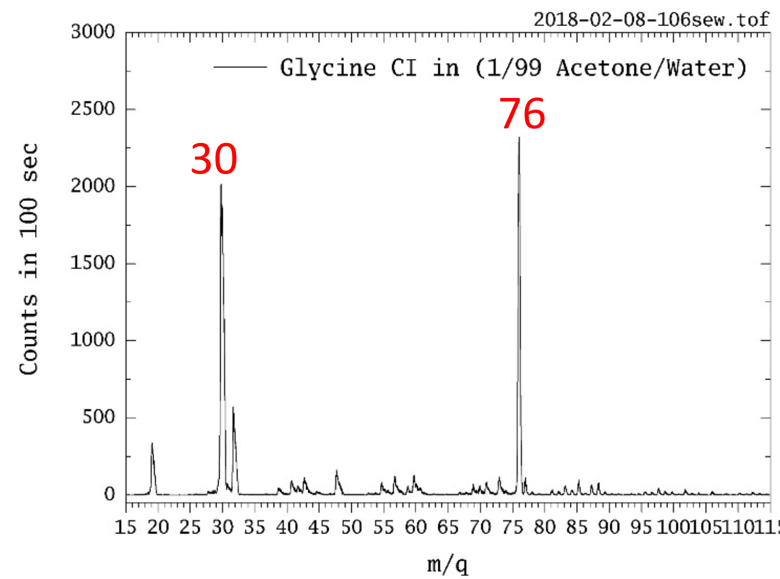


MW: 75 Da
PA: 886.5 kJ/mol

CI: Water



CI: Water/Acetone (99/1)



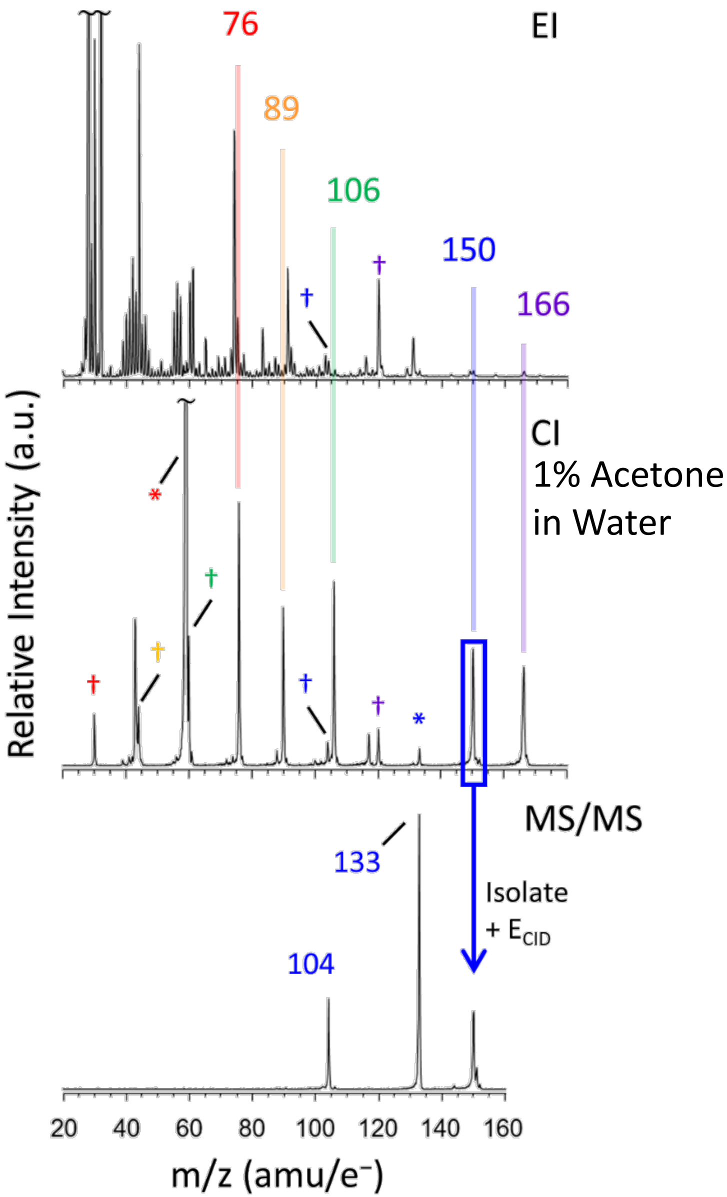
- Adding acetone to a majority water background gas "softens" ionization
- A water:acetone ratio of 99:1 provides best results
  - +/- one order of magnitude also OK
- Could select separate CI reagent for softer ionization of amino acids

$$H_3O^+ + R_{Ac} \longrightarrow R_{Ac}H^+ + H_2O$$

$$R_{Ac}H^+ + A \longrightarrow AH^+ + R_{Ac}$$

Molecule	Proton Affinity (PA, kJ/mol)	ΔPA w/Glycine (kJ/mol)
Water	691	195.5 (2.0 eV)
Acetone	812	74.5 (0.77 eV)

Analysis of Mixtures

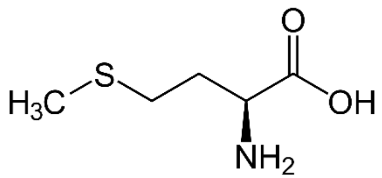


Molecule	Mass (amu)
Glycine	75
Alanine	88
Serine	105
Methionine	149
Phenylalanine	165

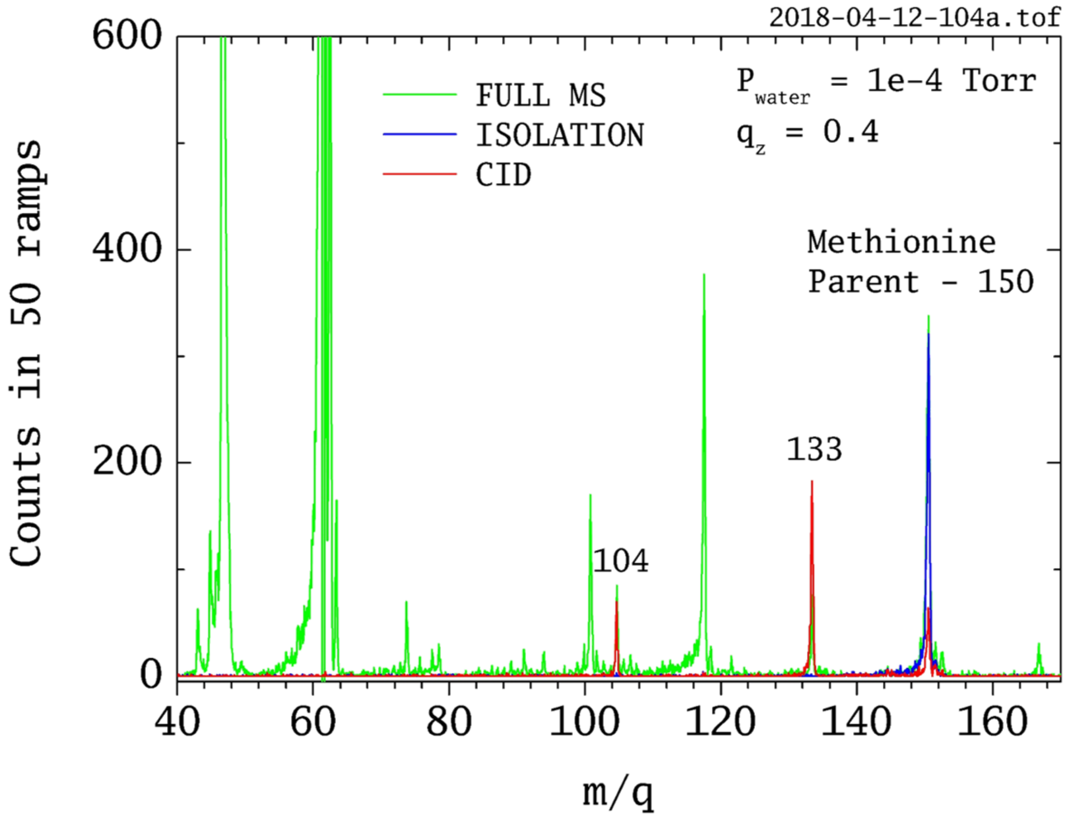
- EI mass spectrum quickly becomes congested with fragment peaks (esp. *m/z* 30 – 100)
- Can differentiate all 5 parent ions
  - Some fragmentation
- Can perform MS/MS for further structural confirmation

MS/MS with Water Collision Gas

CID agent: Water (with 1% Acetone)



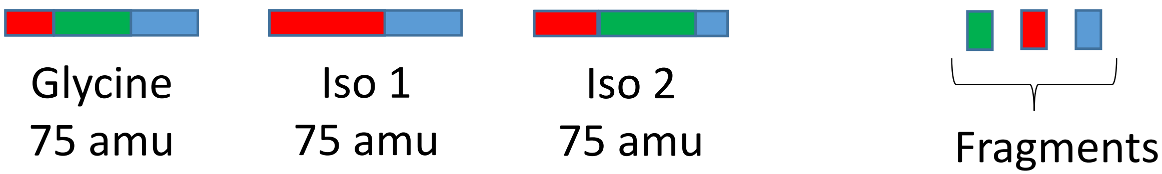
Methionine
MW: 149 Da



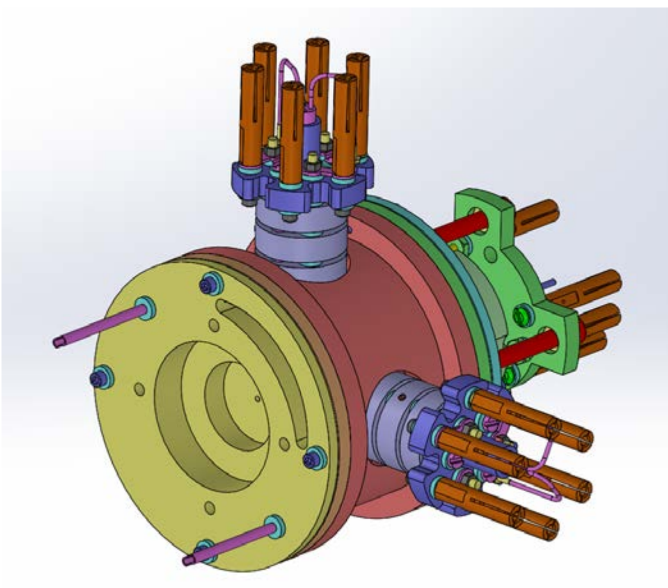
- Minimal losses during isolation
- Good fragmentation efficiency
- Fragments at 133 and 104 amu
  133: Ammonia loss
  104: Formic acid loss
- Works well for all of the amino acids so far
  - Having some issues with fatty acids (lose water before activation)

Next Steps

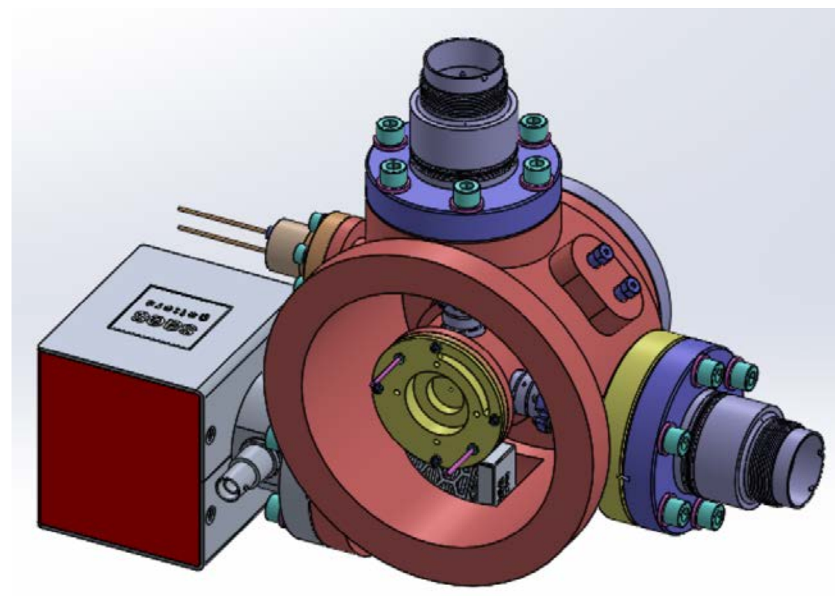
- MS/MS to identify potential confounding isomers in a mixture



- Interface with hypervelocity ice gun

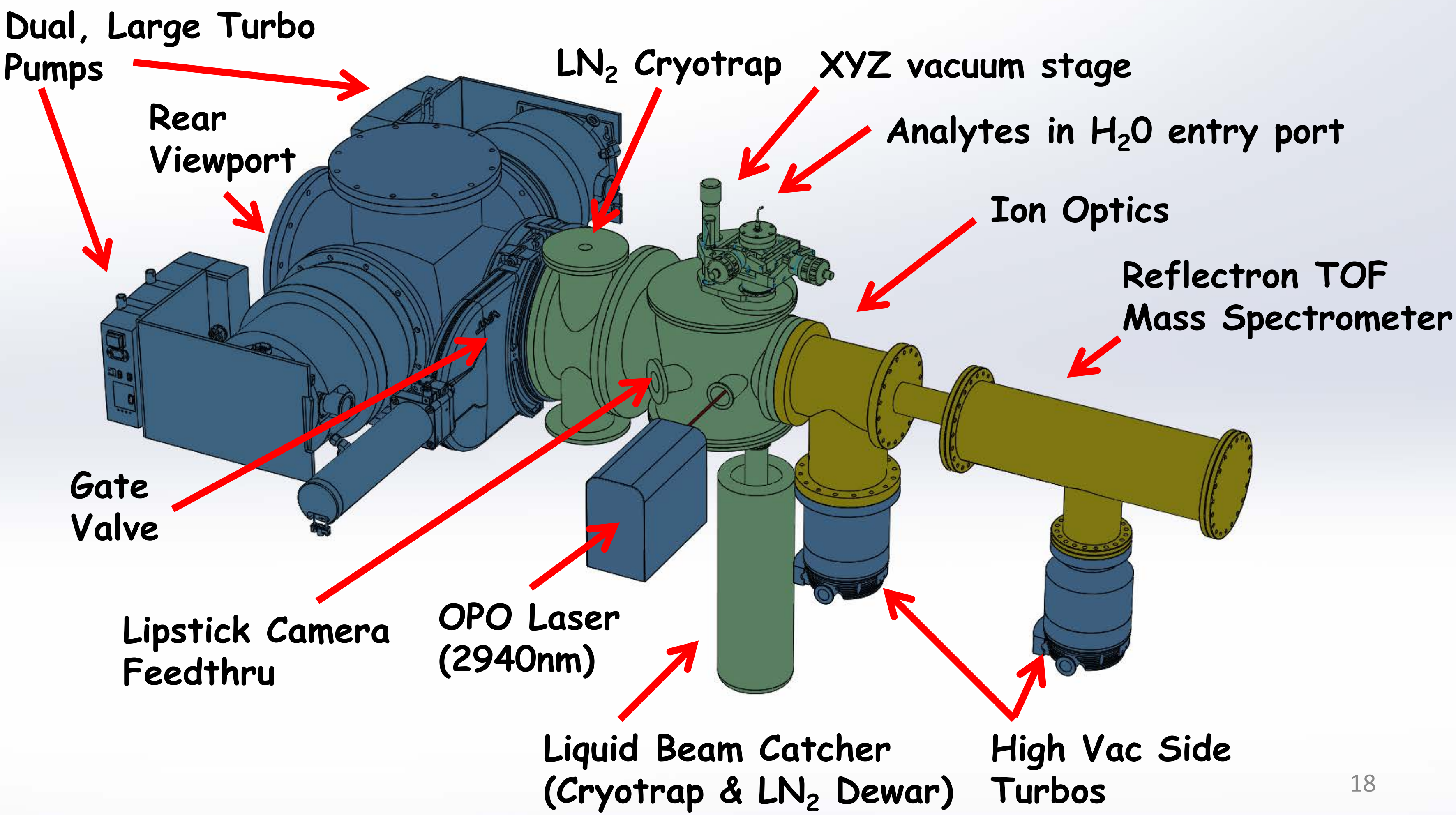


Side-ionization-capable QITMS with hypervelocity input and gas delivery



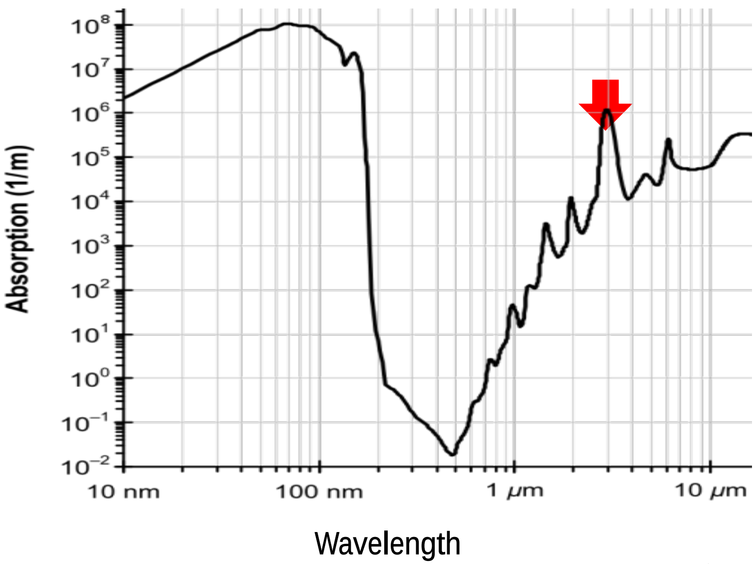
Enclosure optimization for interface to hypervelocity ice gun.

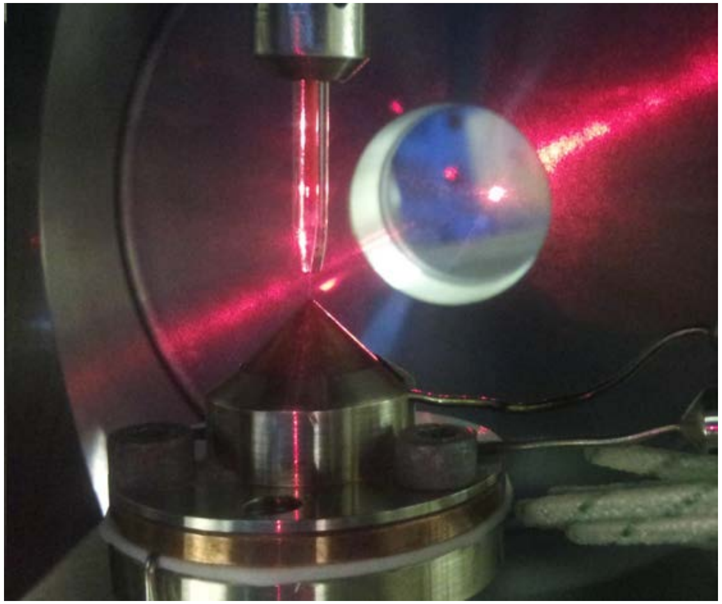
Hypervelocity Ice Gun

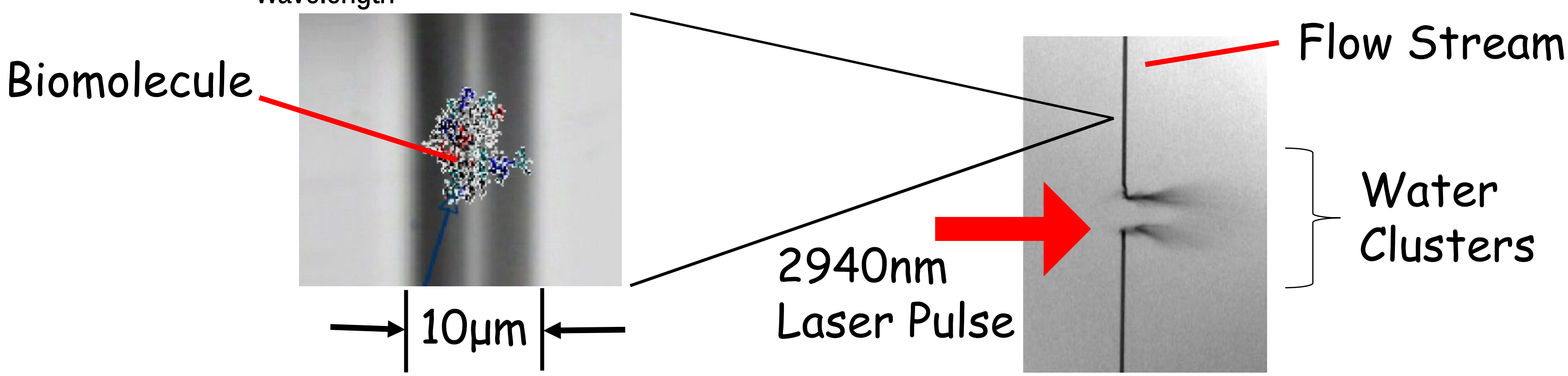


Generating Hypervelocity Ice Grains in the Lab

Absorption Spectrum of Water







IR Laser/Liquid Beam Interactions in the testbed generate neutral and charged particles with mass and velocity distributions analogous to the Enceladus Ice plume/QTIMS interactions.

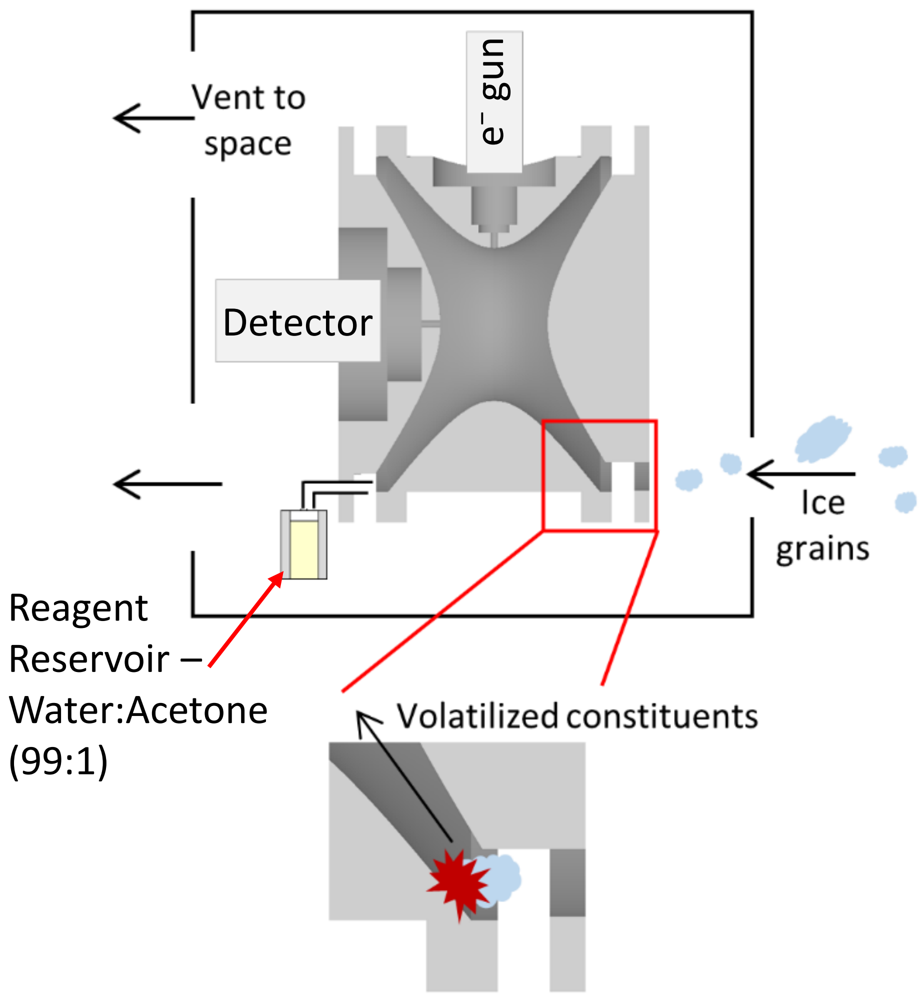
Conclusions

- Soft chemical ionization of amino/fatty acids was achieved in the QIT-MS in water-rich environments like those expected when sampling ice grains at hypervelocity

- A mixture of water:acetone (99:1) is capable of relatively soft ionization of both amino and fatty acids
  - Will continue to search for a lighter reagent with similar proton affinity as acetone
  - Could use a separate reagent for CI of amino acids with reduced fragmentation
  - Effective for mixtures

- The water/acetone mixture has been successfully used as a collision gas for MS/MS

Hypervelocity Ice Sampling Design



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  - Nick Tallarida – Hypervelocity ice (JPL)
  - Rob Hartsock – Hypervelocity ice (JPL)