Paper Spray Ionization under Harsh Environment and Gas Phase Ion Molecule Reaction under Titan Simulate Environment

Anyin Li; Fred Jjunju, Eric Boone, Robert Shellie, Michael Wleklinski, Kerri A. Pratt, R. Graham Cooks

Harsh Environments Always Help Us Understand Science

Nitrogen Unable to Sustain Life

La Chimica in Famiglia (Chemistry in the family), 1886 by Gustavo Milan

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Nomenclature by Antoine Lavoisier

- Azote from the Greek word "ἄζωτος" (azotos) *meaning "lifeless, without life"*
- Azotobacter, bacteria possess nitrogenase enzymes
- Azide N_3^-,
- Hydrazoic acid, HN_3
- Azo compounds,
- Imidazole, triazoles, etc.

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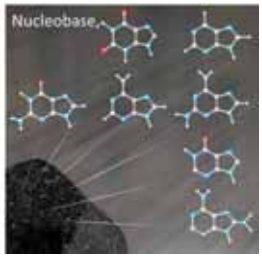
Azote (N) Containing Molecules, Jigsaw Piece for Life

Lavoisier probably didn't expect this



Nitrogen Chemistry Before Life???

Burton, A. S. et al. *Chem. Soc. Rev.*, 2012, **41**, 5459-5472
http://jonlieffmd.com/wp-content/uploads/2013/03/NitrogenCycle.png

4

Titan, Haze Aerosols of N-organics

Transporter room. We are in position above Titan.

The crew of the USS Enterprise hides behind Titan, using Titan's haze and Saturn's magnetic field to avoid being detected by Narada, which is on its way to attack Earth.

Image from Star Trek (2009)

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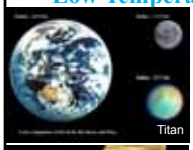
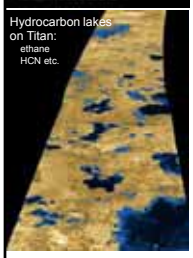
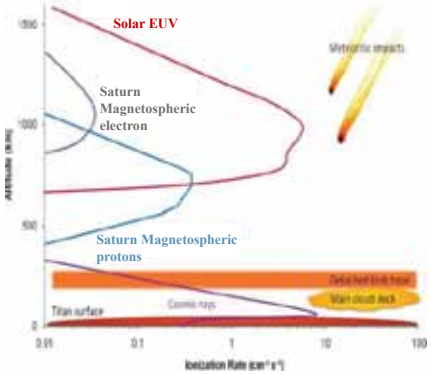
Titan Harsh Environments, Low Temperature, nonpolar liquids & High energy



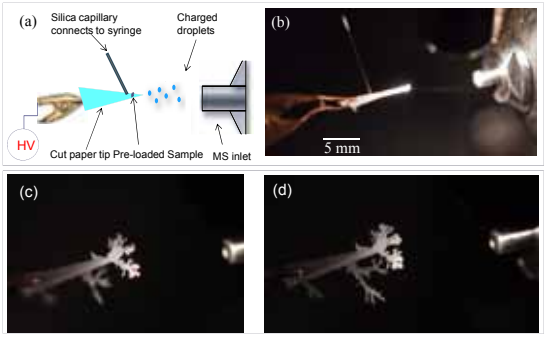




1. J. H. Waite, et. al. , *Science* ***2007, 316, 870-875.*** 2. Cordier, D.; Mousis, O.; Lunine, J. I.; Lavvas, P.; Vuitton, V. *Astrophysical Journal Letters* ***2009, 707, L128.*** 3. Cable, M. L.; Horst, S. M.; Hodyss, R.; Beauchamp, P. M.; Smith, M. A.; Willis, P. A., *Chem. Rev.* ***2012, 112 (3), 1882-1909.***

6

Spray ionization of non-polar solvents



Ionization and MS analysis of both polar and non-polar analytes was achieved.

Li, A.; Wang, H.; Ouyang, Z.; Cooks, R. G. *Chem. Commun.* ***2011, 47, 2811.***

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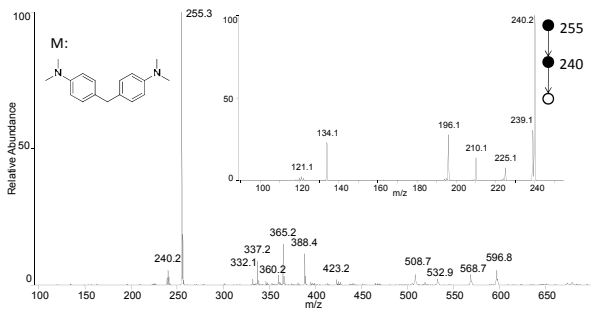
Low Temperature Paper Spray Ionization

8

Nitrogen containing aromatics in hexane analyzed by paper spray



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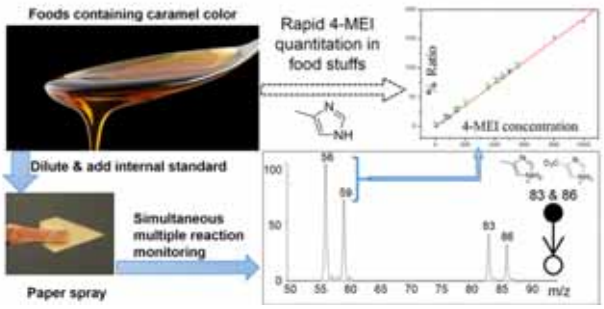
Direct Analysis of Viscous Liquids



Li, A., Wei, P., Hsu, H. C., & Cooks, R. G. *Analyst* (2013)

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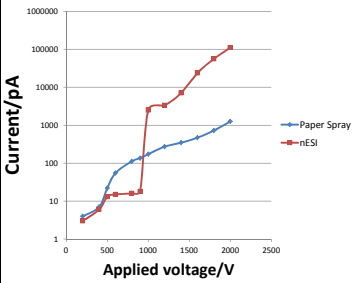
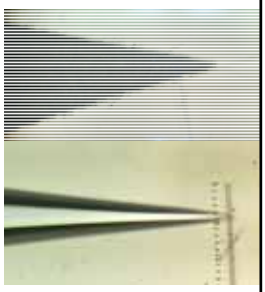
Paper spray, why it works, Surface area and sharp emitters





Freezing of solvents does not shut off the spray current for paper spray, only limit it to around 100 pA

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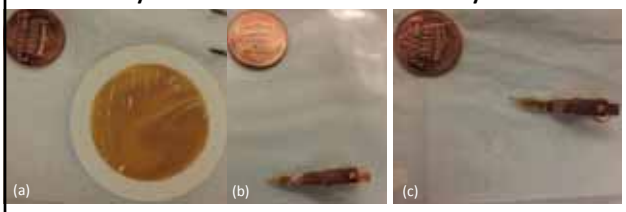
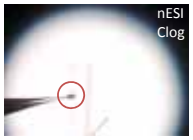
Synthetic tholin and analysis





In Collaboration with Joshua Sebree, NASA

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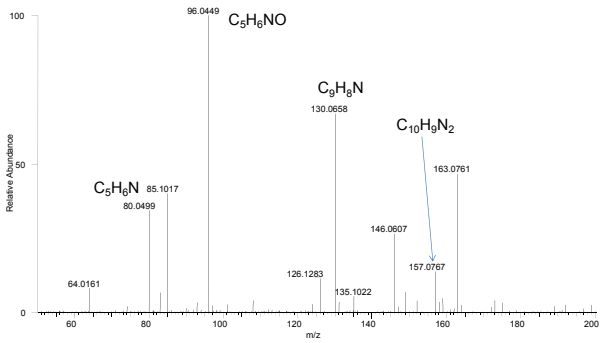
Positive PS spectrum of Tholin sample



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Polybrominated dipheny ethers (PBDE)

- 209 congeners
- Originally used as flame retardants
- Persistent in the environment
- Typical analysis by GC-MS, GC-MS/MS

Emerging threat in Antarctica

- Enclosed dusty spaces, low ventilation (to avoid heat loss)
- High use of flame retardant materials (safety)

Metabolites thought to be more toxic (hydroxylated)

- Not amenable to GC analysis (require derivatization)
- Paperspray-MS, **5 ppb** LOD

14 *Professor Robert Shellie*

UTAS

University of Michigan

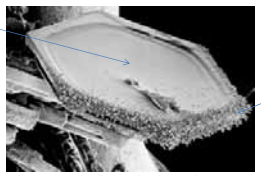
Collaboration: Eric Boone & Prof. Kerri Pratt

Surface Snow Chemistry

Goal: Develop a method that allows chemical analysis of the snow surface

Question: What organic species exist on the surface of snow grains, and could they be photochemical precursors to trace organic gases above the snowpack?

In the center/bulk?



On the surface?

Photo: USDA Beltsville Agricultural Research Center

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Method Development

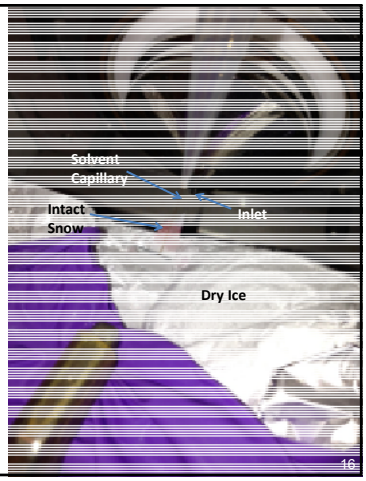
Challenges:

- Preventing the snow from melting, while preventing the mass spectrometer inlet from freezing
- Low concentrations of organic compounds in snow

Method:

- Application of paper spray mass spectrometry (Liu et al., 2010) to examine the snow surface
- The snow surface is solvated from the solid snow into the paper and then ionized

Liu et al., *Analytical Chemistry*, **2010**, 82 (6), 2463–2471.



Eric Boone & Kerri Pratt (Univ. of Michigan)

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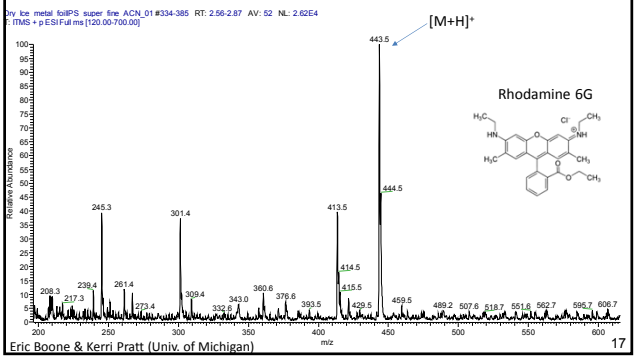
First Tests

Artificial snow/ice pellets were made by freezing a solution of Rhodamine 6G with a concentration of 3 ppm



Eric Boone & Kerri Pratt (Univ. of Michigan)

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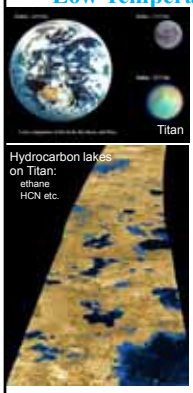
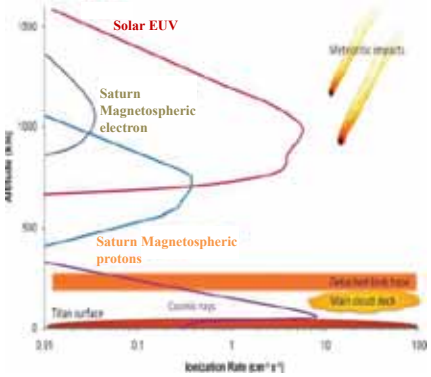
Titan Harsh Environments, Low Temperature, nonpolar liquids & High energy





1. J. H. Waite, et. al. , *Science* ***2007, 316, 870-875.*** 2. Cordier, D.; Mousis, O.; Lunine, J. I.; Lavvas, P.; Vuitton, V. *Astrophysical Journal Letters* ***2009, 707, L128.***
3. Cable, M. L.; Horst, S. M.; Hodyss, R.; Beauchamp, P. M.; Smith, M. A.; Willis, P. A., *Chem. Rev.* ***2012, 112 (3), 1882-1909.***

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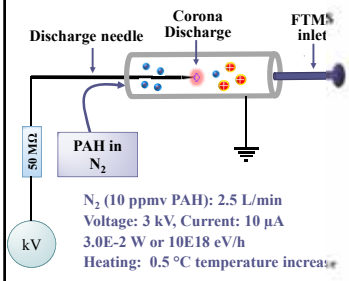
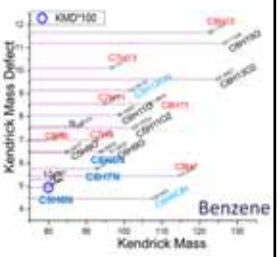
Simulating Chemistry in Harsh Environment Cold Plasma Discharge



N_2 (10 ppmv PAH): 2.5 L/min
Voltage: 3 kV, Current: 10 µA
3.0E-2 W or 10E18 eV/h
Heating: 0.5 °C temperature increase



Reproduces:
1) Magnetospheric electron and secondary electrons
2) UV irradiation, 337 and 391 nm for nitrogen plasma

Hydrocarbon grows and have N incorporated.

1. Cable, M. L., et al., *Chem. Rev.* ***2012, 112 (3), 1882-1909.***
2. Chang, J. S.; Maezono, I., *Journal of Physics D-Applied Physics* ***1988, 21 (6), 1023-1024.***

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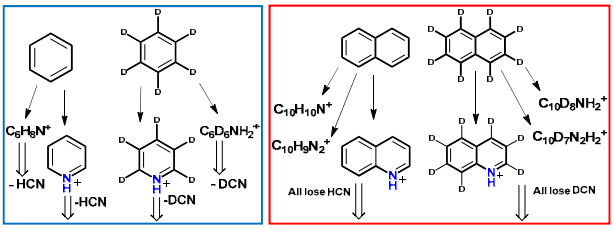
PAHs Transformed to PANHs in N_2 Plasma



Corona discharge with N_2

Collision induced dissociation

All fragmentation loses HCN whose lost H was from *sp*^{2} carbon.

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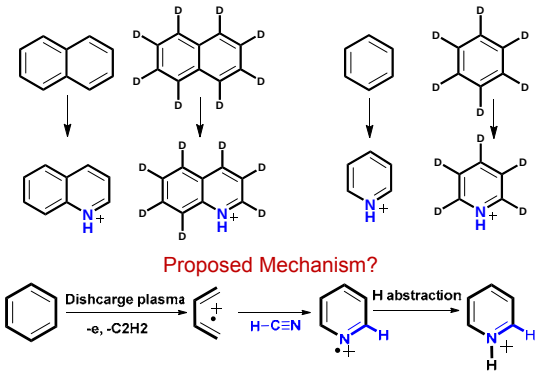
From PAHs to PANHs, Mechanism?



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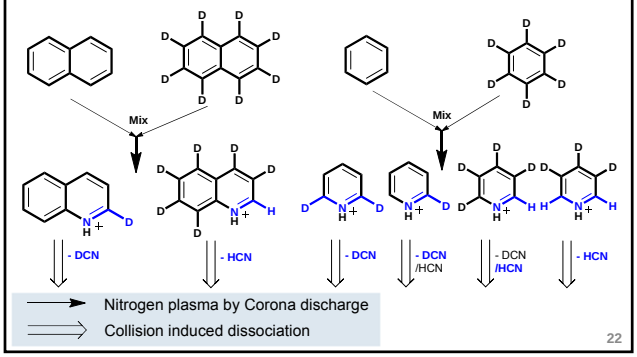
Try to Prove the Mechanism

New ions observed upon mixing



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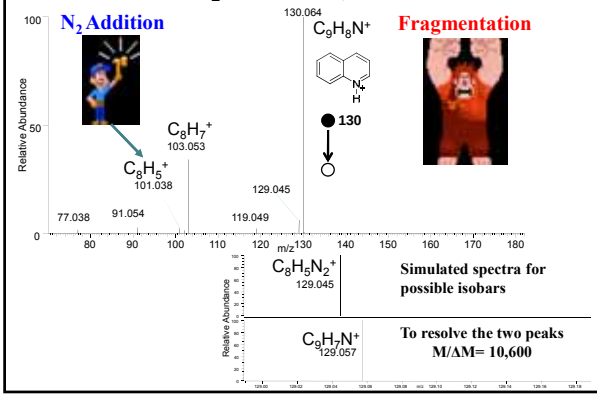
Active N_2 Chemistry without e^-, hν



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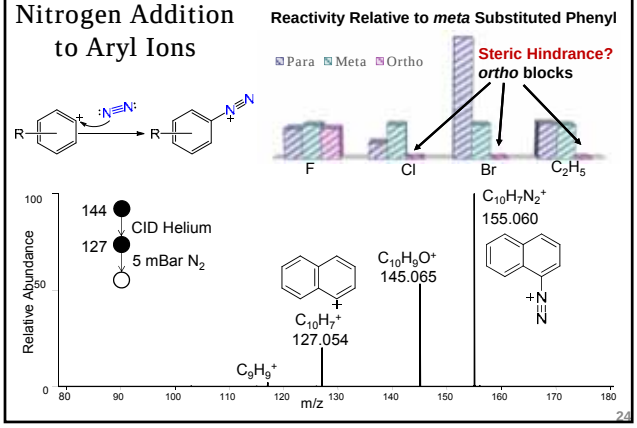
Nitrogen Addition to Aryl Ions



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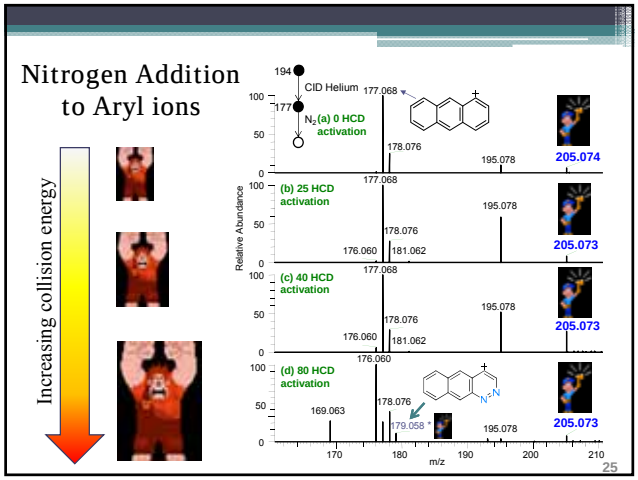
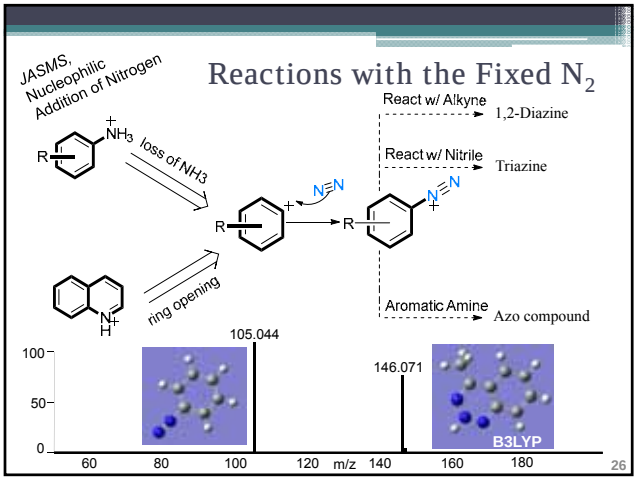
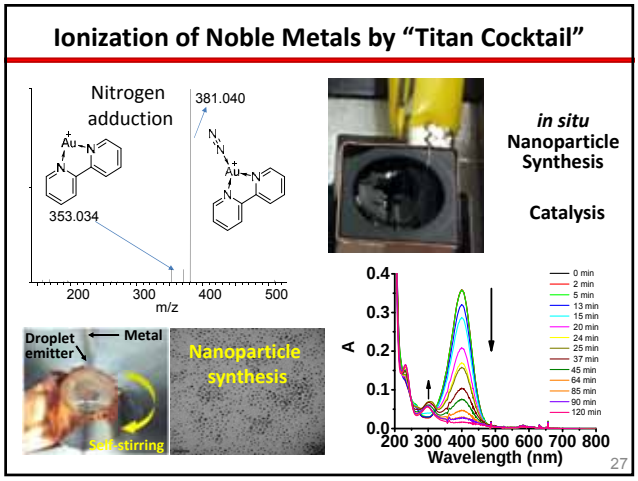

Nitrogen Addition to Aryl ions
Increasing collision energy
CID Helium
N2 (a) 0 HCD activation
(b) 25 HCD activation
(c) 40 HCD activation
(d) 80 HCD activation
Relative Abundance
m/z
205.074
205.073
25


JASMS, Nucleophilic Addition of Nitrogen
Reactions with the Fixed N2
loss of NH3
ring opening
React w/ Alkyne
1,2-Diazine
React w/ Nitrile
Triazine
Aromatic Amine
Azo compound
105.044
146.071
B3LYP
m/z
26


Ionization of Noble Metals by "Titan Cocktail"
Nitrogen adduction
381.040
353.034
m/z
in situ Nanoparticle Synthesis
Catalysis
Droplet emitter
Metal
Self-stirring
Nanoparticle synthesis
A
Wavelength (nm)
27


Dorota
Josh Wiley
Aston Labs 2012
ACS
R. B. Wetherill Laboratory of Chemistry
Thanks!
NASA-PIDDP NNX12AB16G
NSF 0848652 and DBI 0852740
DOE DE-FG02-06ER15807
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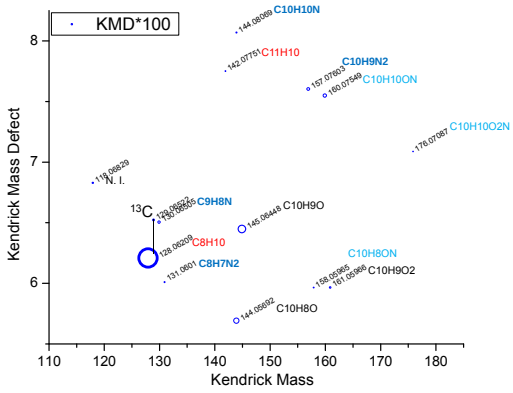
Possible Question # 0

- What other species are formed in the Plasma

Naphthalene transformed by cold plasma



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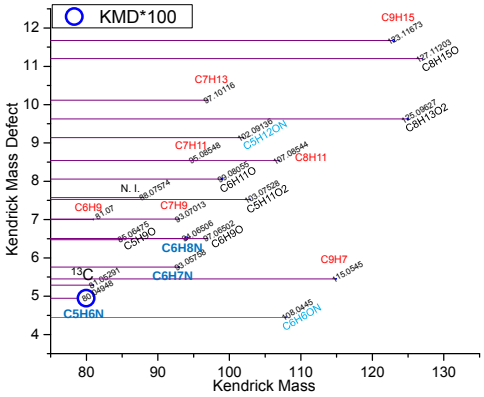
Benzene transformed by cold plasma



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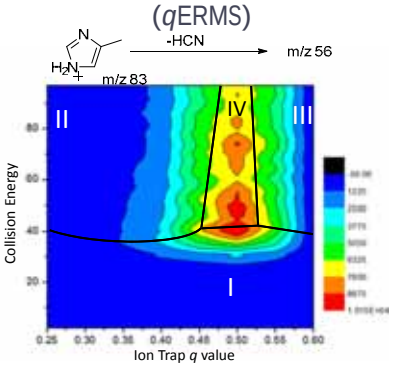
Possible Question # 1

- How do you know N is in the aromatic ring?

N in the aromatic ring? *q*-value and energy resolved tandem MS (*q*ERMS)



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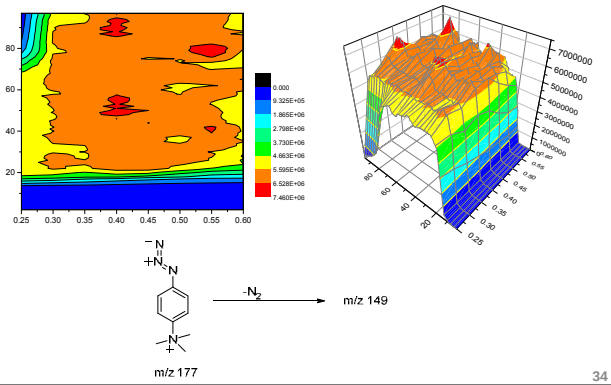
Triazine, Breaking Single Bond



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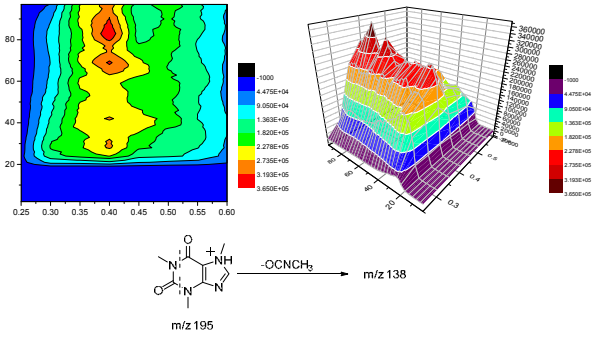
Caffeine, opening non-Aromatic ring



loss of methyl isocyanate, RDA

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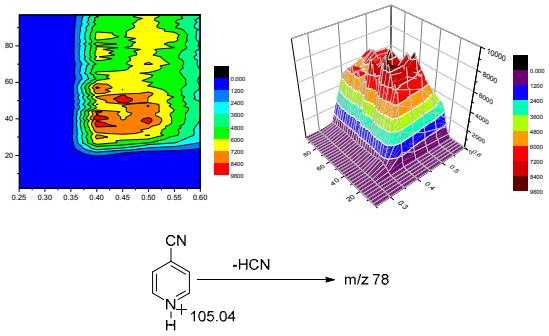
4-Cyanopyridine, Breaking Single Bonds



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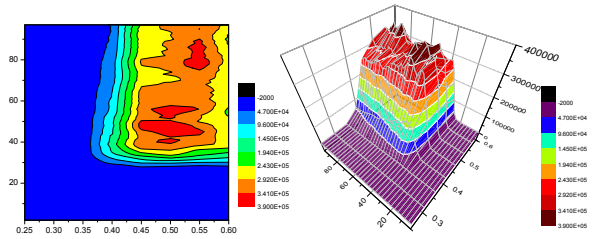
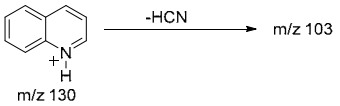
Quinoline, Opening Aromatic Ring





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Possible Question # 2

- Where the HCN is from?

HCN production from hydrocarbon and N_2 in positive discharge plasmsa, a Known Fact

Hydrocarbon + discharge → HCN

One of the proposed routes:

$$CH + N_2 \longrightarrow HCN + N$$

1. Suhr, H., *Angewandte Chemie International Edition in English* ***1972, 11 (9), 781-792.***
2. Drost, H.; Behlke, H.; Rutkowsky, J.; Spangenberg, H. J., *Zeitschrift Fur Anorganische Und Allgemeine Chemie* ***1976, 426 (2), 189-197.***
3. Thompson, W. R.; Henry, T. J.; Schwartz, J. M.; Khare, B. N.; Sagan, C., *Icarus* ***1991, 90 (1), 57-73.***
4. Borucki, W. J.; Giver, L. P.; Mckay, C. P.; Scattergood, T.; Parris, J. E., *Icarus* ***1988, 76 (1), 125-134.***

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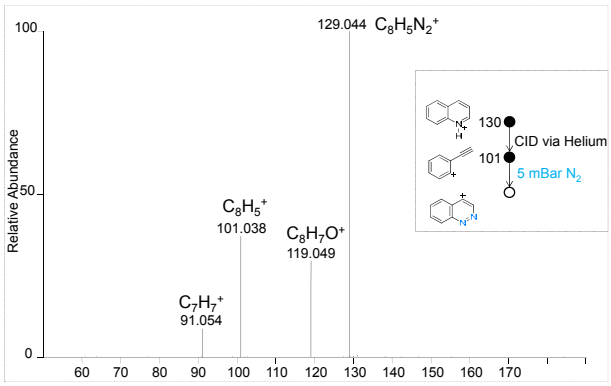
Possible Question # 3

- Is it really N2 adds to m/z 101?

Isolated Ion-molecule reaction



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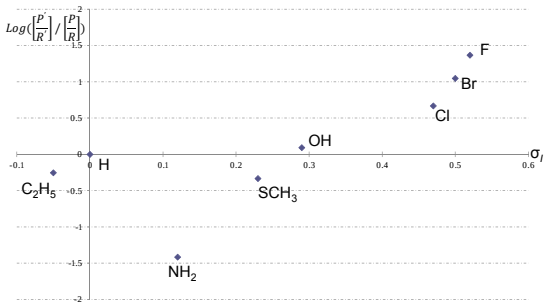
Possible Question # 4

- How do the reactivities compare with each other?
- Other influences on the reactivity

Inductive effects on the reactivity



para-substituted influence

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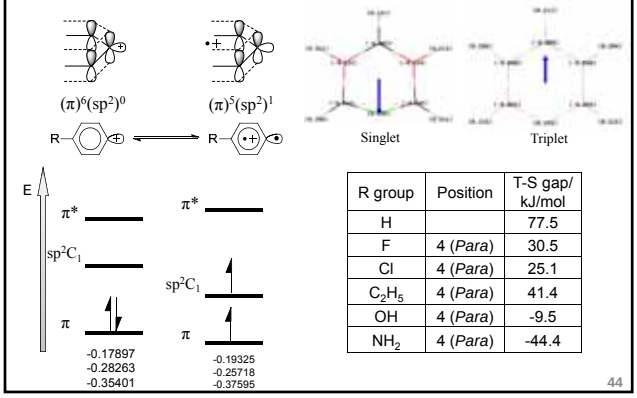
Spin Isomerization of aryl cations, T-S gap



R group	Position	T-S gap/ kJ/mol
H		77.5
F	4 (*Para*)	30.5
Cl	4 (*Para*)	25.1
C_2H_5	4 (*Para*)	41.4
OH	4 (*Para*)	-9.5
NH_2	4 (*Para*)	-44.4

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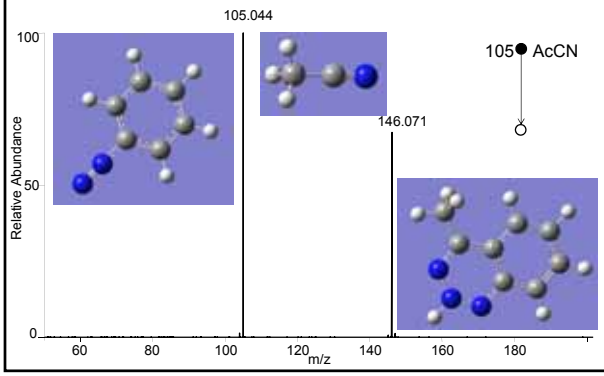
Possible Question # 5

- Reactions of diazoniums?

Diazonium Reaction with Acetonitrile



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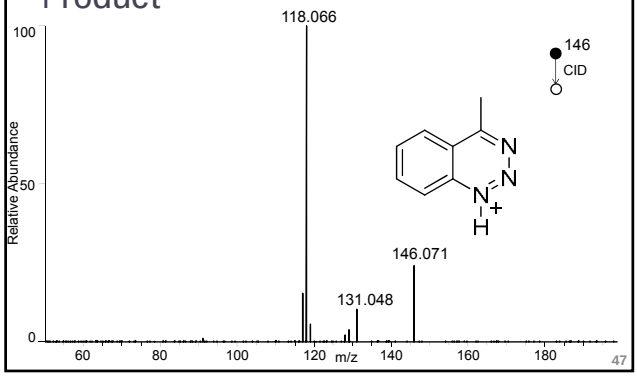
Fragmentation of the AcCN Product



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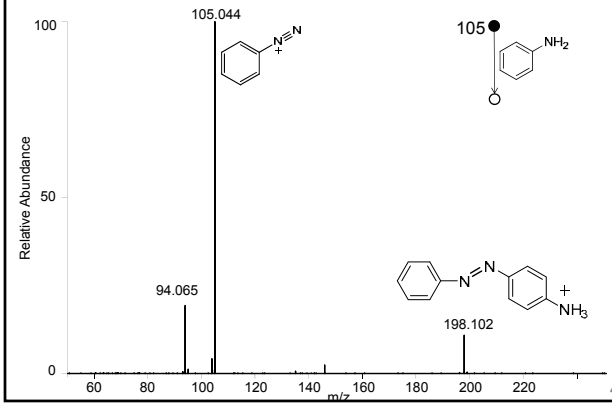
Diazonium Reaction with analine



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Diazonium Reaction with 3-octyne