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AFRL

Heterogeneous Catalysis of Ionic Liquids

Steven D. Chambreau, Ph.D.

AFRL/RQRP and Jacobs Technology, Inc.



Introduction

Motivation

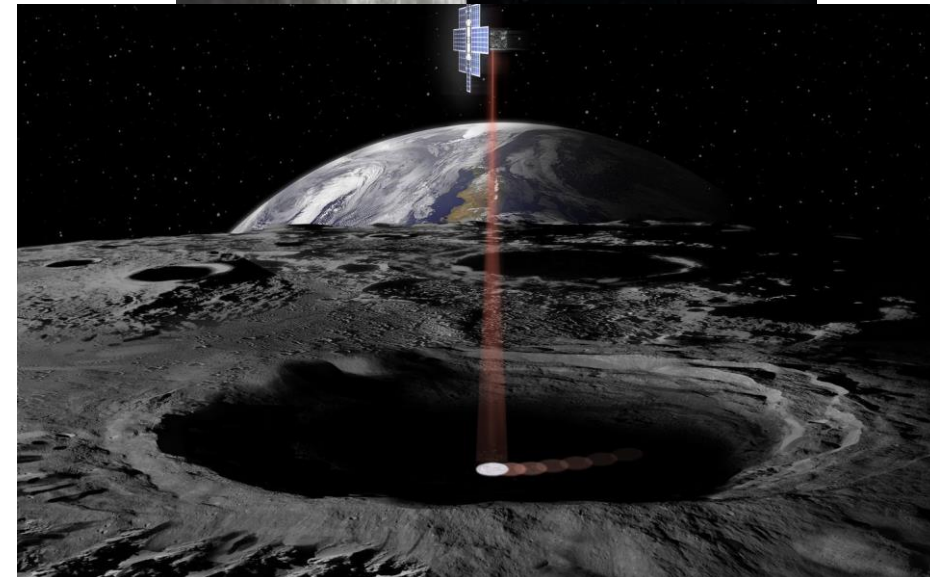
- Replacement for highly toxic fuels!
 - Improved performance.
 - Environmentally “greener”
- New fuels (ionic liquids) have:
 - Extremely low vapor pressures.
 - High energy density.
 - Low flammability.
- Catalytic Ignition involves:
 - Dissociative chemisorption and recombination.
 - Rapid heating: vaporization and thermal decomposition.
 - Ignition.
- How to predict ignition properties?





Green Propellants (GPIM) NASA/AFRL Partnership

- Satellite launched in June 2019!
Successful mission!



Catalytic Decomposition of Hydroxylammonium Nitrate Ionic Liquid: Enhancement of NO Formation

Steven D. Chambreau,[†] Denisia M. Popolan-Vaida,^{‡,§} Ghanshyam L. Vaghjiani,^{*,||} and Stephen R. Leone^{‡,§}

[†]ERC, Inc., Edwards Air Force Base, California 93524, United States

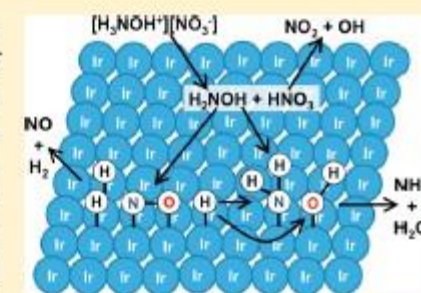
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^{||}In-Space Propulsion Branch, Rocket Propulsion Division, Aerospace Systems Directorate, Air Force Research Laboratory, AFRL/RQRS, Edwards Air Force Base, California 93524, United States

Supporting Information

ABSTRACT: Hydroxylammonium nitrate (HAN) is a promising candidate to replace highly toxic hydrazine in monopropellant thruster space applications. The reactivity of HAN aerosols on heated copper and iridium targets was investigated using tunable vacuum ultraviolet photoionization time-of-flight aerosol mass spectrometry. The reaction products were identified by their mass-to-charge ratios and their ionization energies. Products include NH₃, H₂O, NO, hydroxylamine (HA), HNO₃, and a small amount of NO₂ at high temperature. No N₂O was detected under these experimental conditions, despite the fact that N₂O is one of the expected products according to the generally accepted thermal decomposition mechanism of HAN. Upon introduction of iridium catalyst, a significant enhancement of the NO/HA ratio was observed. This observation indicates that the formation of NO via decomposition of HA is an important pathway in the catalytic decomposition of HAN.



Thermal and Catalytic Decomposition of 2-Hydroxyethylhydrazine and 2-Hydroxyethylhydrazinium Nitrate Ionic Liquid

Steven D. Chambreau, Denisia M. Popolan-Vaida, Oleg Kostko, Jae Kyoo Lee, Zhenpeng Zhou, Timothy A. Brown, Paul Jones, Kuanliang Shao, Jingsong Zhang, Ghanshyam L. Vaghjiani,* Richard N. Zare, and Stephen R. Leone

Cite This: <https://doi.org/10.1021/acs.jpca.1c07408>

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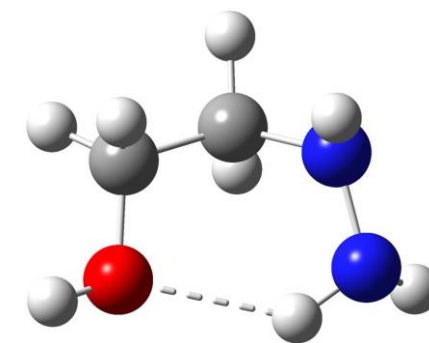
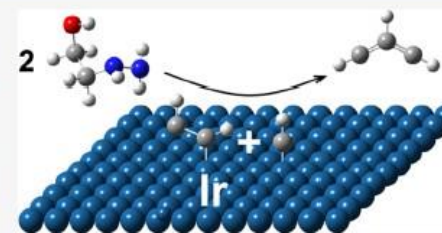
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Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: To develop chemical kinetics models for the combustion of ionic liquid-based monopropellants, identification of the elementary steps in the thermal and catalytic decomposition of components such as 2-hydroxyethylhydrazinium nitrate (HEHN) is needed but is currently not well understood. The first decomposition step in protic ionic liquids such as HEHN is typically the proton transfer from the cation to the anion, resulting in the formation of 2-hydroxyethylhydrazine (HEH) and HNO_3 . In the first part of this investigation, the high-temperature thermal decomposition of HEH is probed with flash pyrolysis (<1400 K) and vacuum ultraviolet (10.45 eV) photoionization time-of-flight mass spectrometry (VUV-PI-TOFMS). Next, the investigation into the thermal and catalytic decomposition of HEHN includes two mass spectrometric techniques: (1) tunable VUV-PI-TOFMS (7.4–15 eV) and (2) ambient ionization mass spectrometry utilizing both plasma and laser ionization techniques whereby HEHN is introduced onto a heated inert or iridium catalytic surface and the products are probed. The products can be identified by their masses, their ionization energies, and their collision-induced fragmentation patterns. Formation of product species indicates that catalytic surface recombination is an important reaction process in the decomposition mechanism of HEHN. The products and their possible elementary reaction mechanisms are discussed.



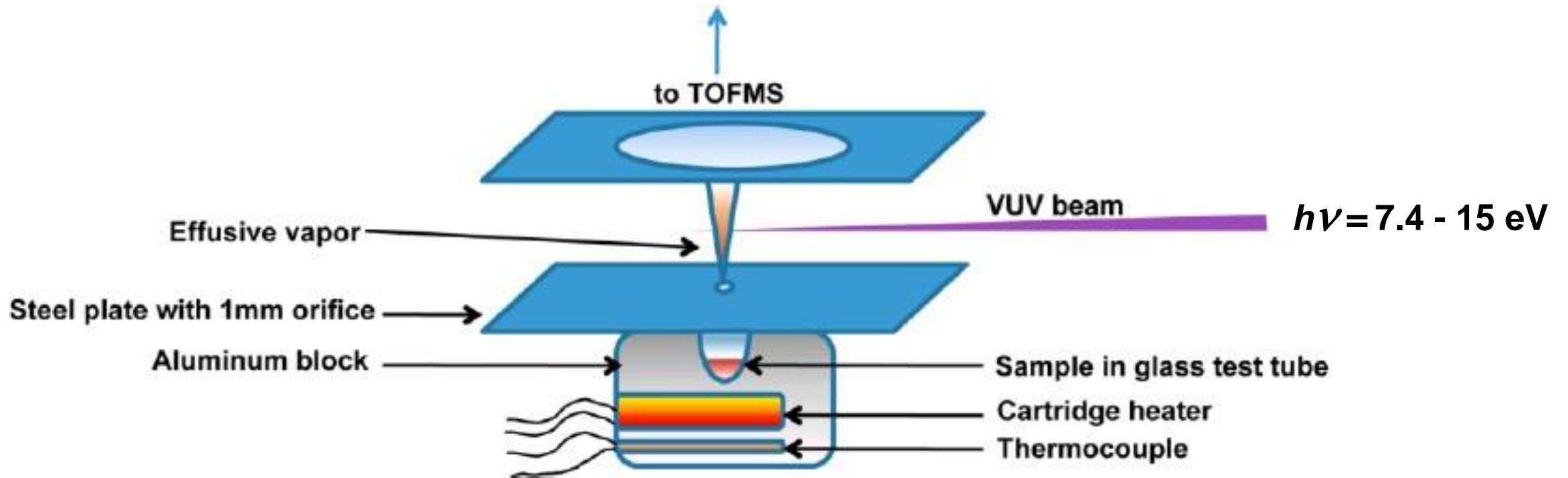
J. Phys. Chem. Lett. 2022

DOI: 10.1021/acs.jpca.1c07408

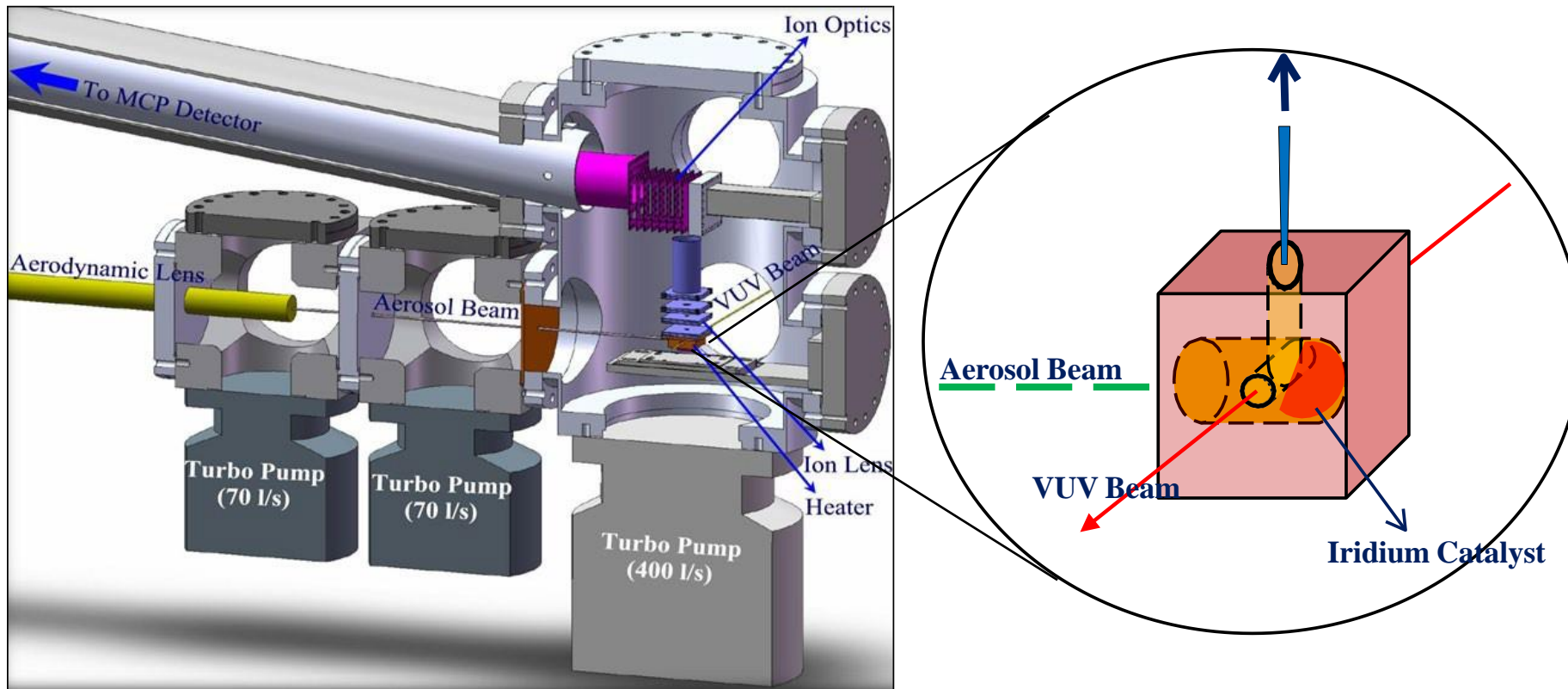


Experimental: Tunable VUV-PI-TOFMS

Tunable VUV-PI-TOFMS: Effusive Source



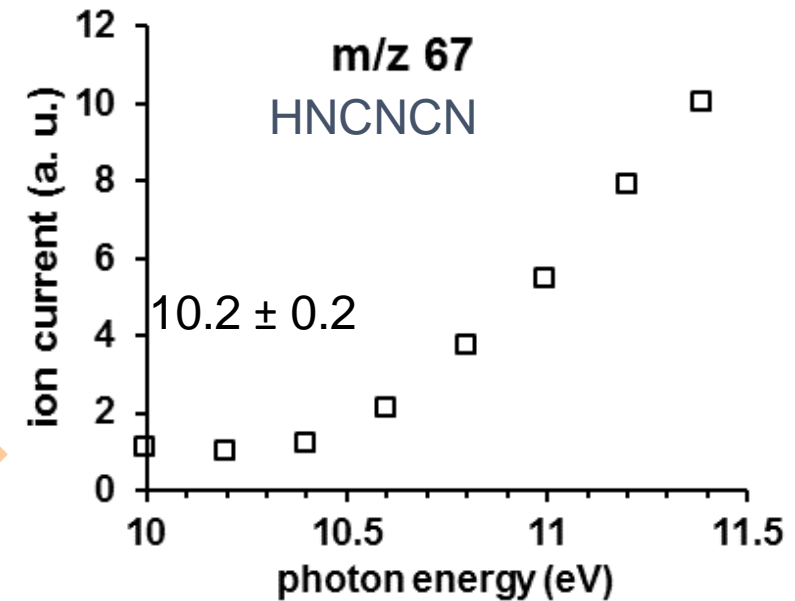
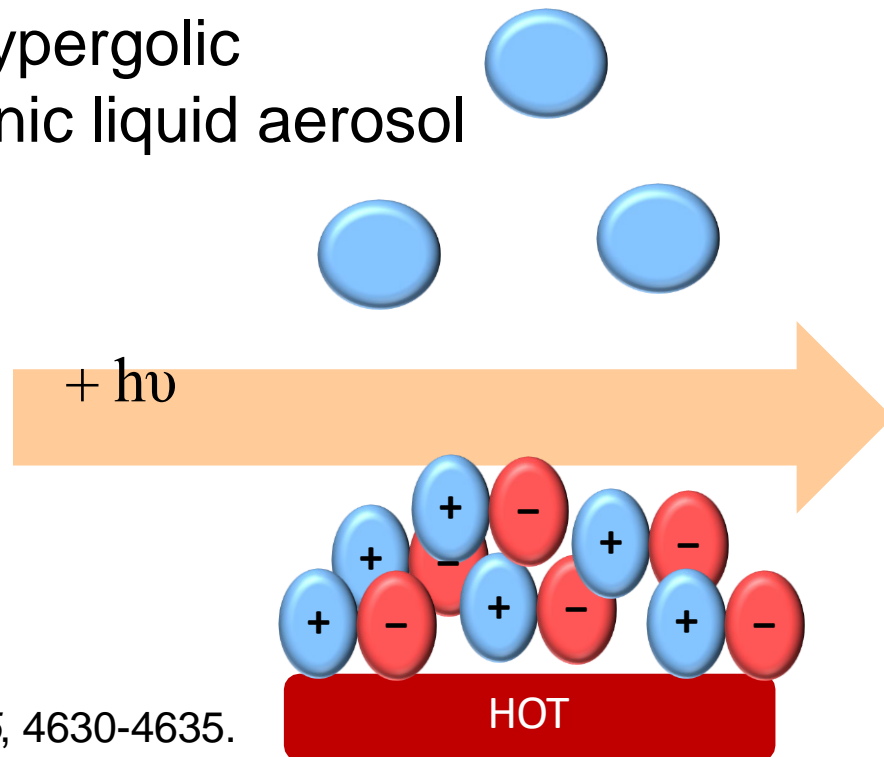
Aerosol Tunable VUV-PI-TOFMS



Monitoring Isolated Ion Pairs

- Use it to **study reaction kinetics** of ‘hypergolic ionic liquid reaction with an oxidizer’

Hypergolic
Ionic liquid aerosol



J. Phys. Chem. A **2011**, *115*, 4630-4635.

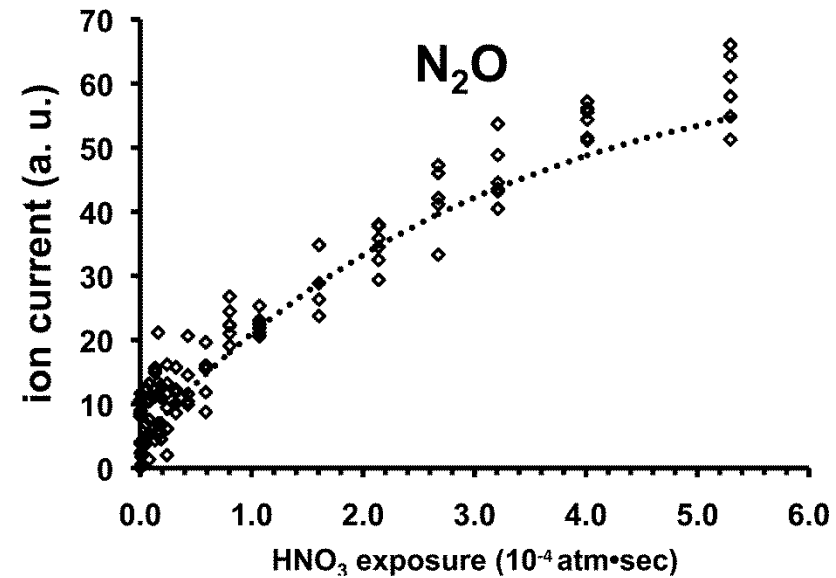
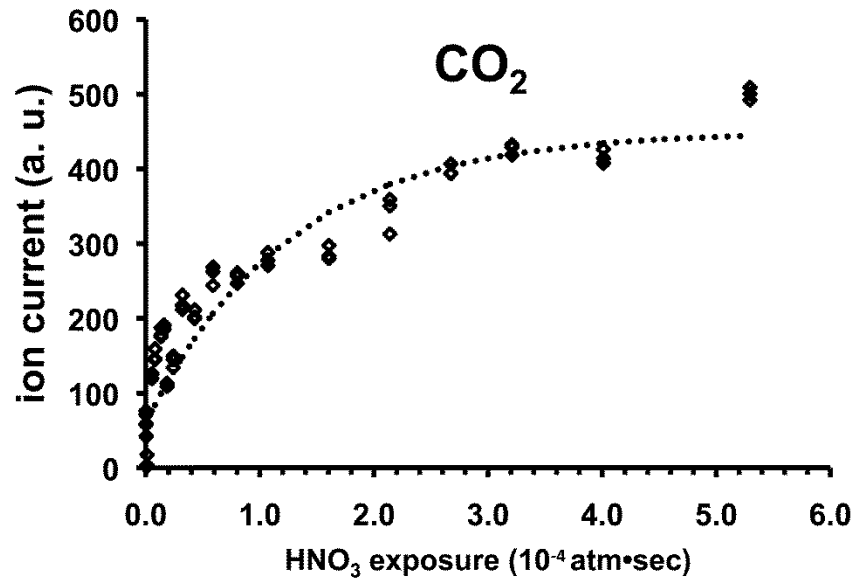


Aerosol Kinetics Data

IL + H¹⁵NO₃

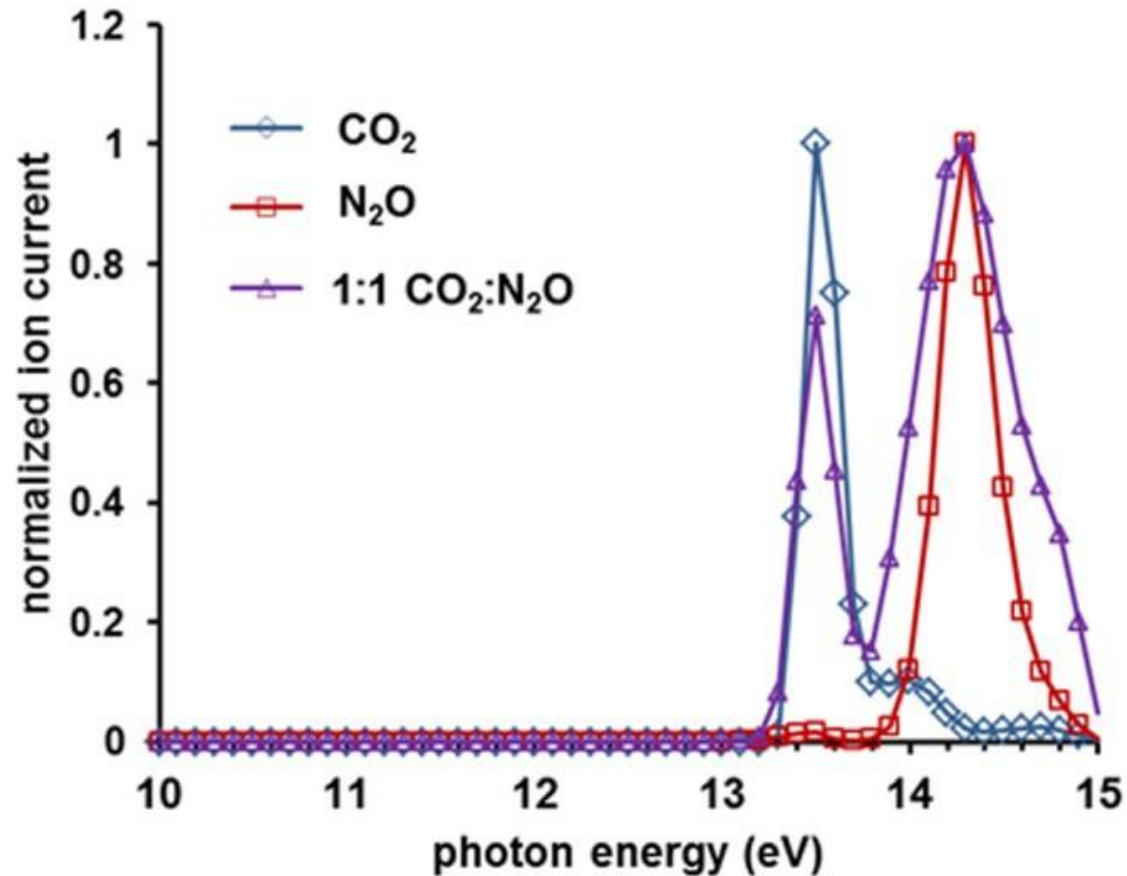
CO₂ at 13.5 eV

¹⁵NNO at 14.3 eV





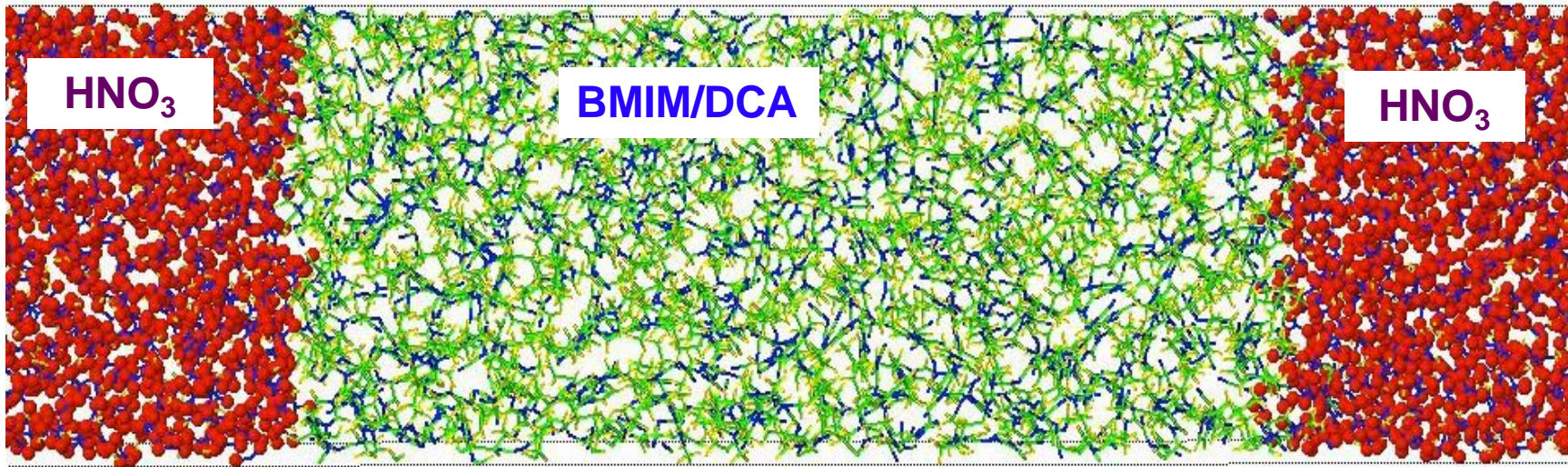
N₂O vs CO₂ detection



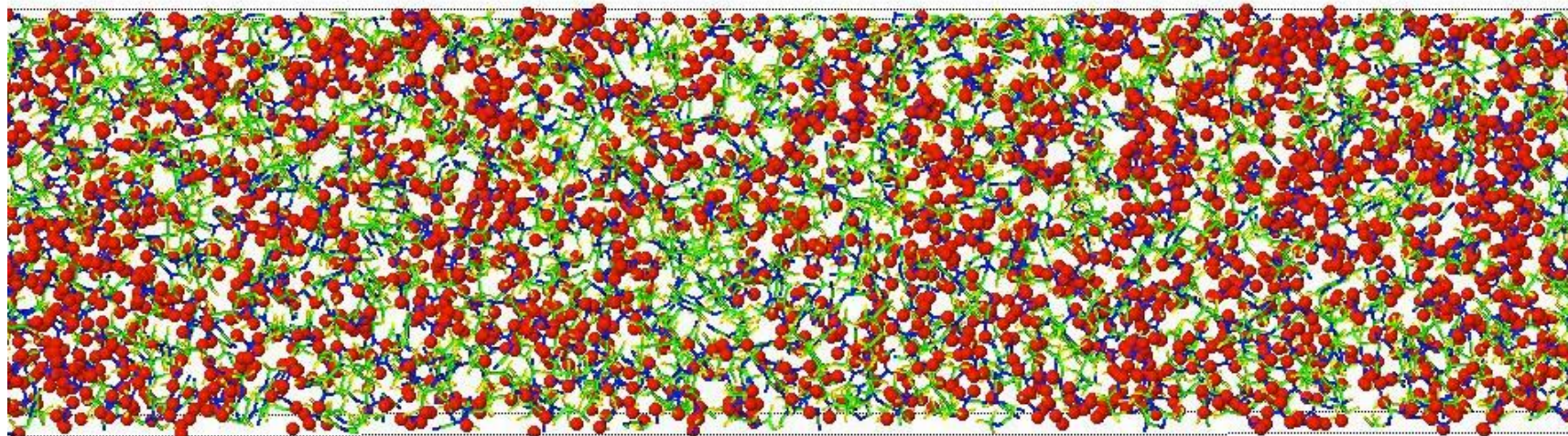
High resolution PIE curves for N₂O (blue), CO₂ (red) and a 1:1 mixture of N₂O to CO₂ (purple).

MD Simulations of IL/oxidizer Interphases: Liquid-liquid

t = 0



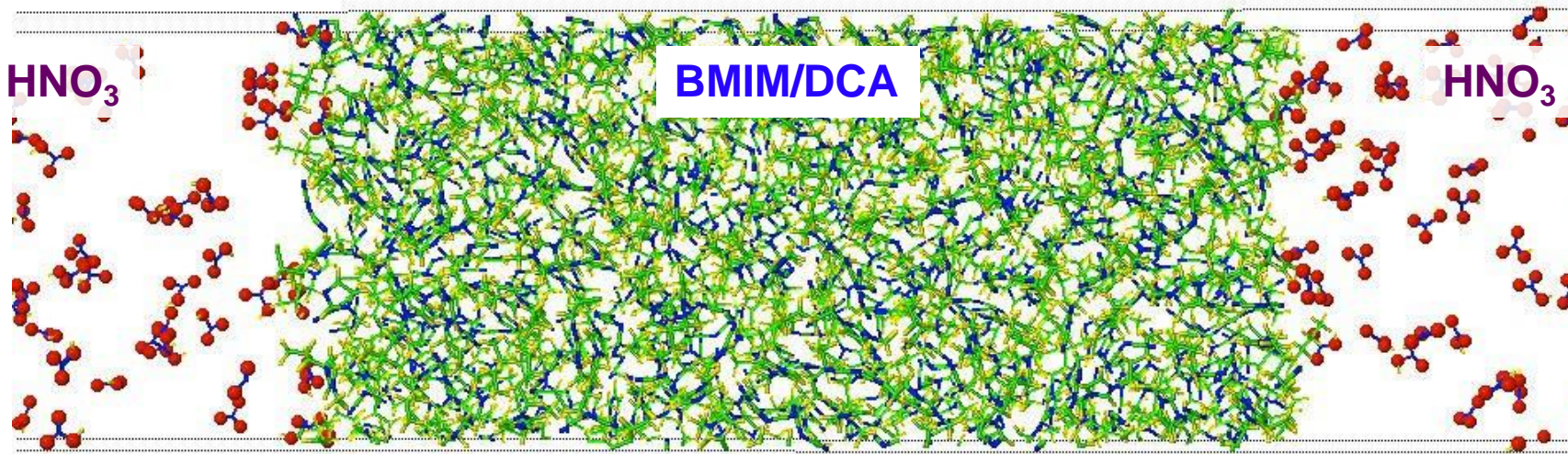
t = 6 ns



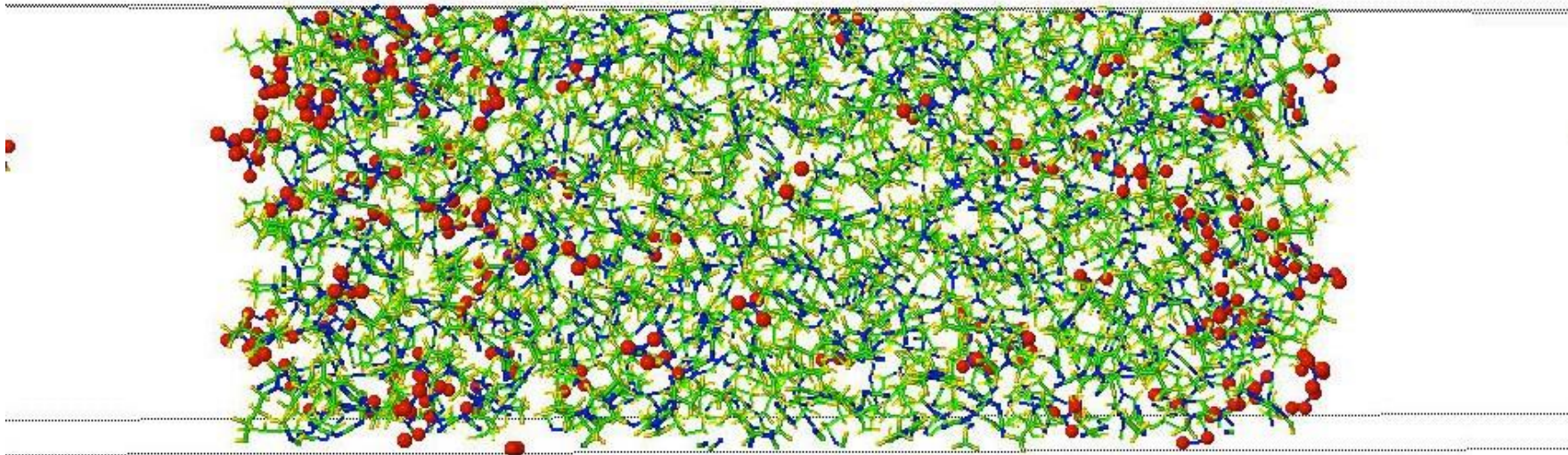
in liquid/liquid systems, mixing is rapid! *J Phys Chem A* 2014, 48, 11116

MD Simulations of IL/oxidizer Interphases: Liquid-gas

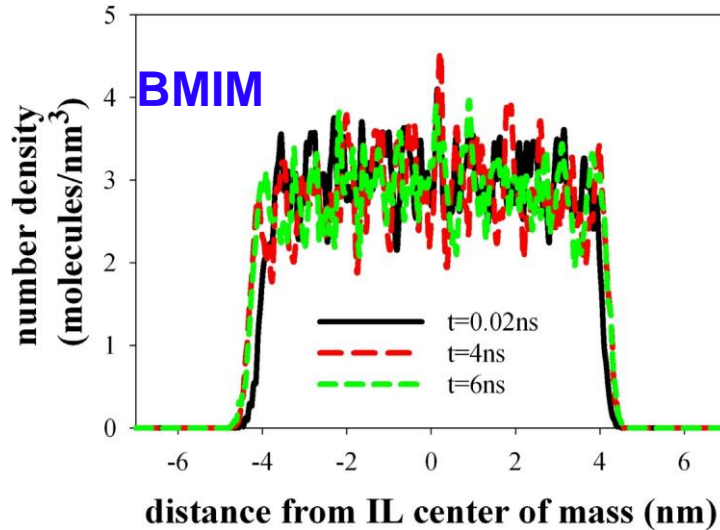
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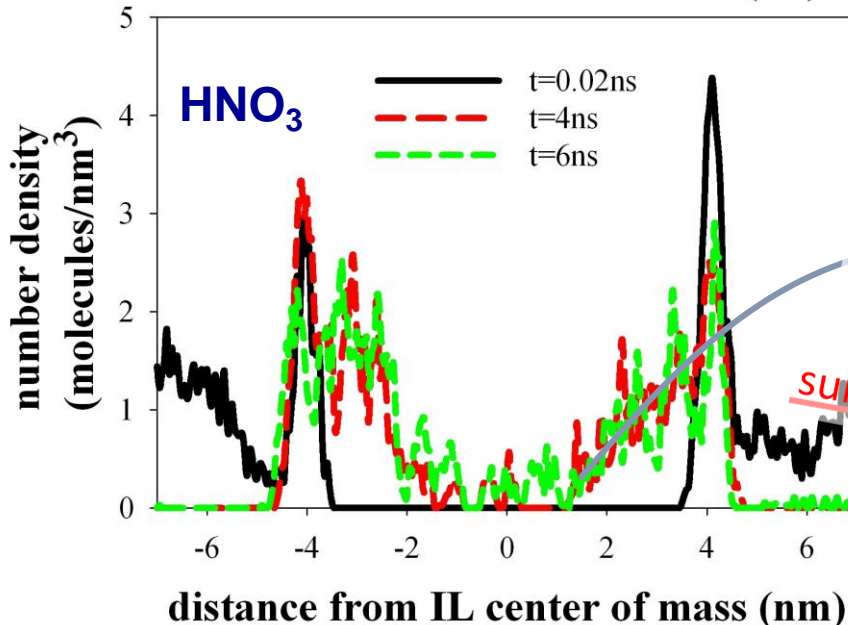
t = 6 ns



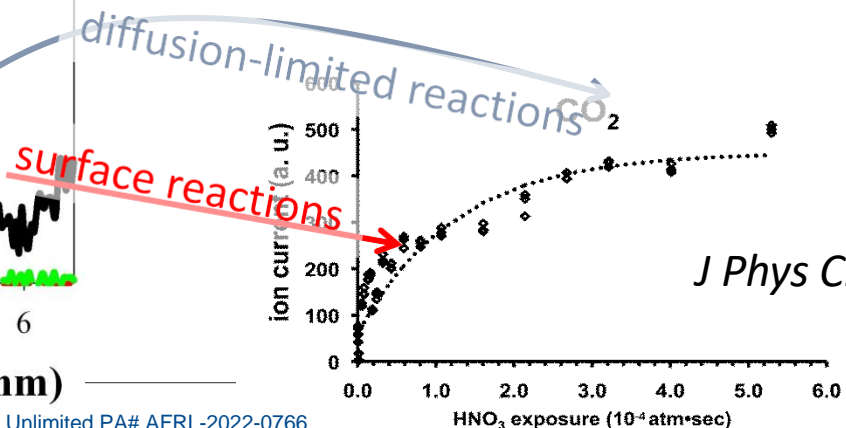
MD Simulations of IL/oxidizer Interphases: Liquid-gas



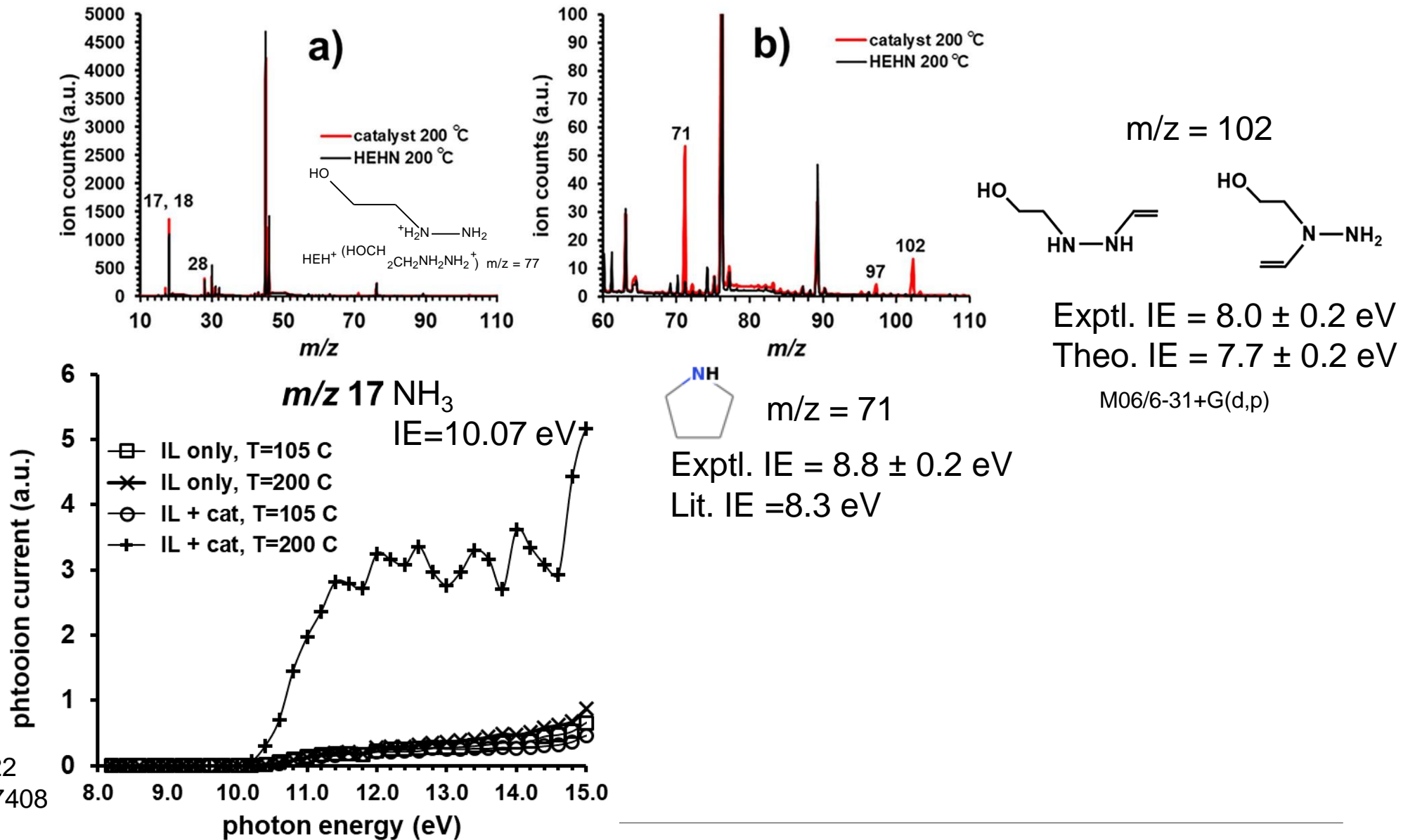
At the liquid-gas interphase HNO₃ quickly adsorbs to the surface and then slowly diffuses to the bulk.



There is a certain concentration of HNO₃ at the surface that system would like to maintain to reduce the surface tension



J Phys Chem A **2014**, 48, 11116

HEHN Effusive Source, Total Ion Current Mass Spectra: $\Sigma(7.4-15 \text{ eV})$ 

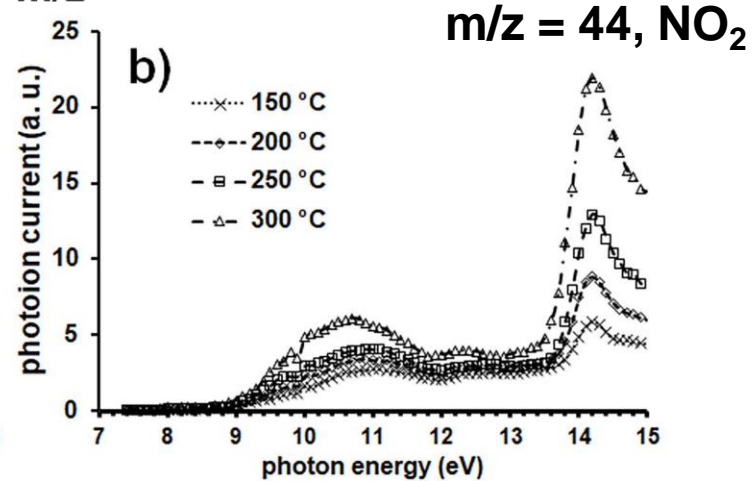
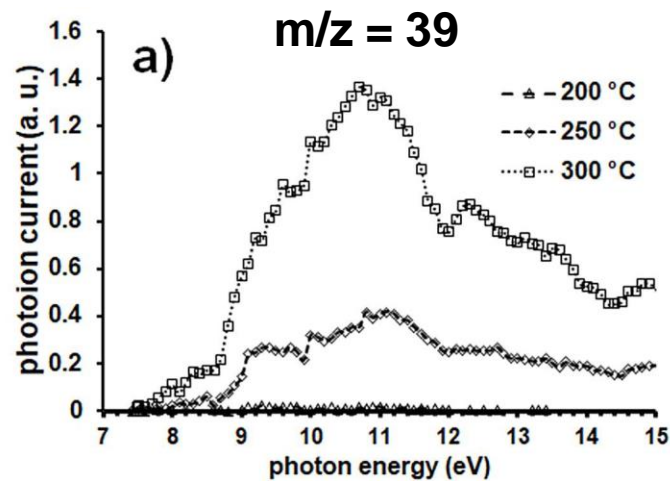
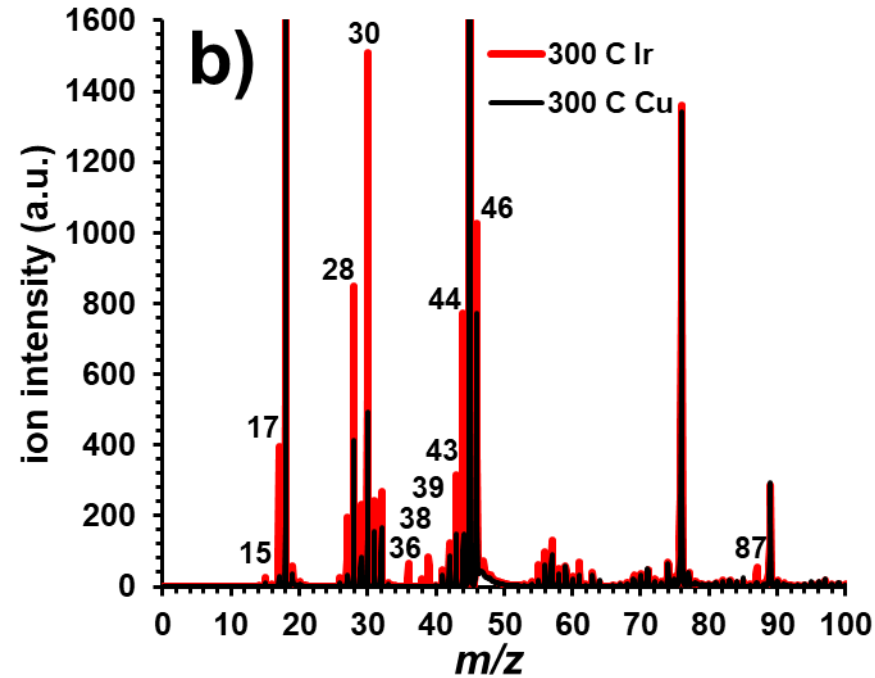
J. Phys. Chem. Lett. 2022

DOI: 10.1021/acs.jpca.1c07408

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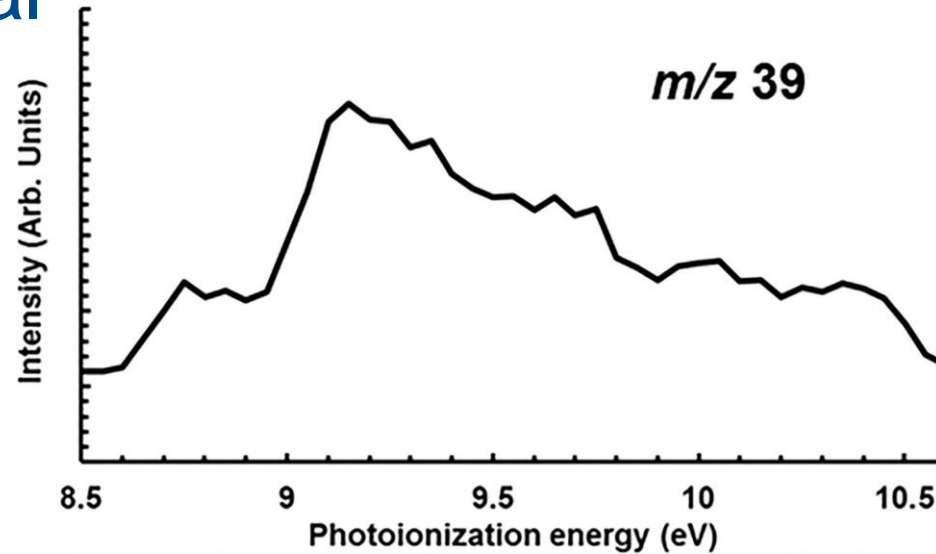
HEHN Aerosol Source, Total Ion Current Mass Spectra: $\Sigma(7.4-15 \text{ eV})$



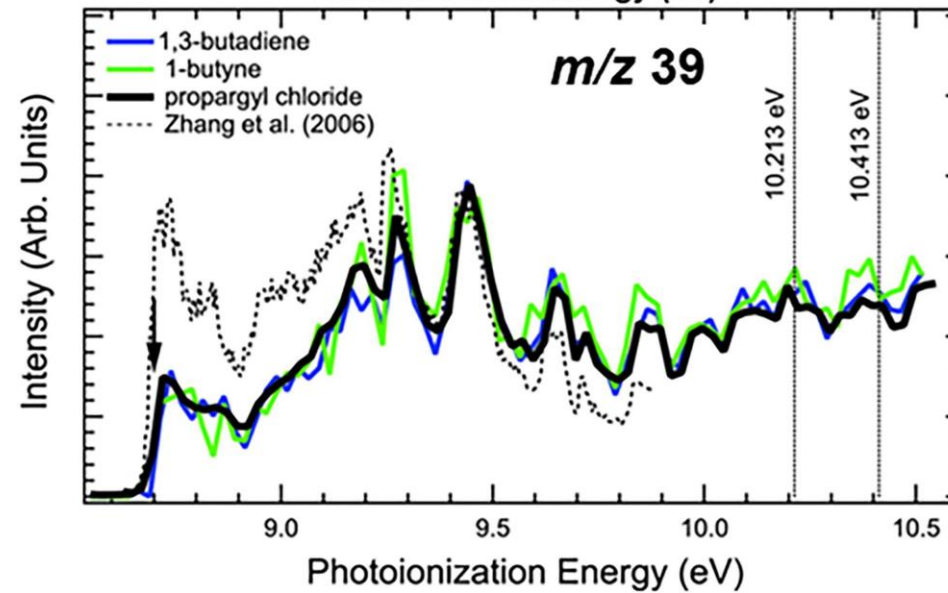
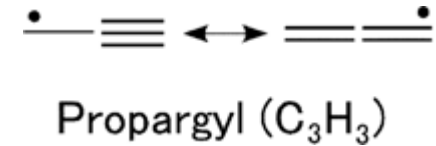
J. Phys. Chem. Lett. 2022
DOI: 10.1021/acs.jpca.1c07408

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Propargyl Radical



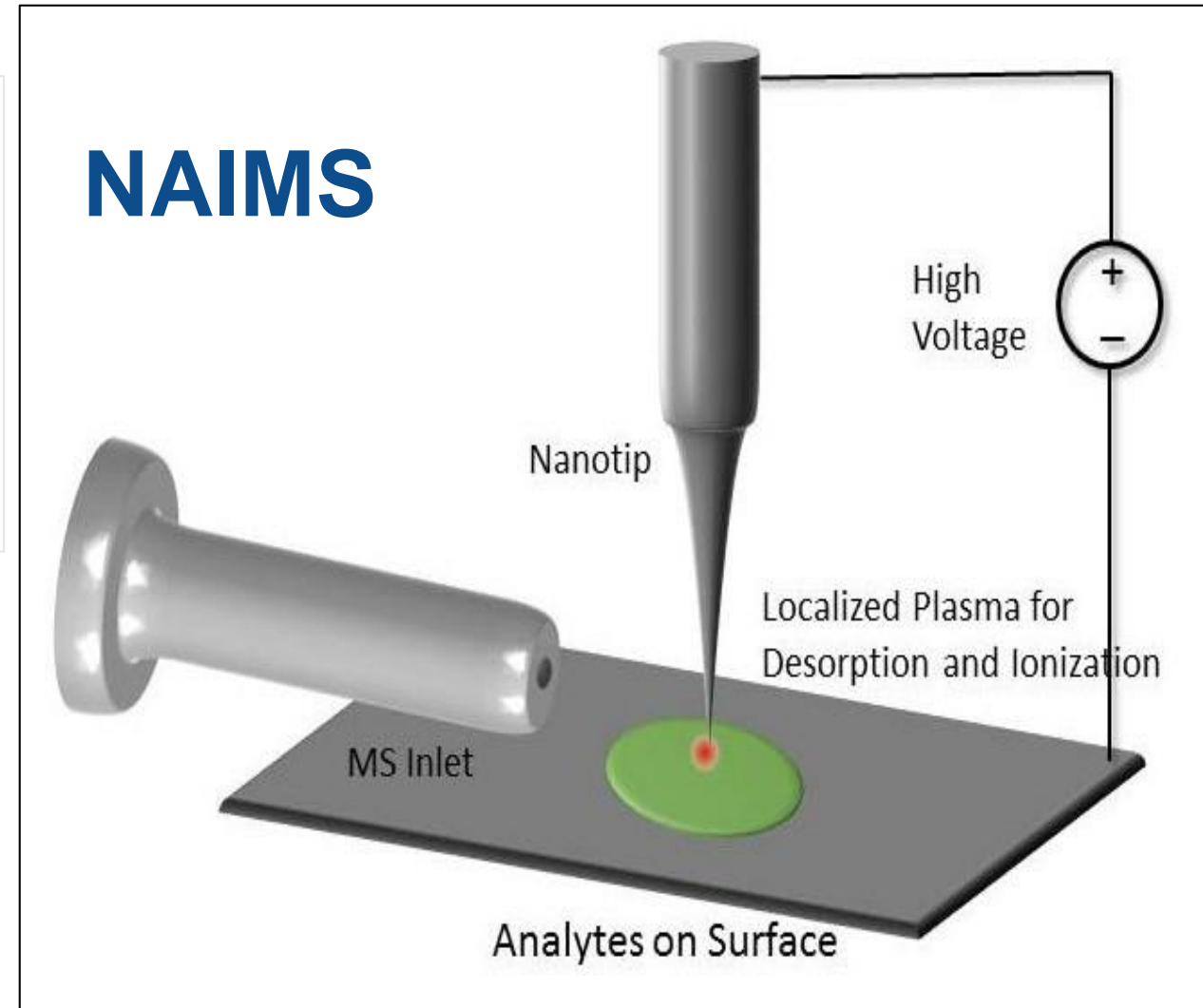
m/z = 39, C₃H₃ propargyl radical



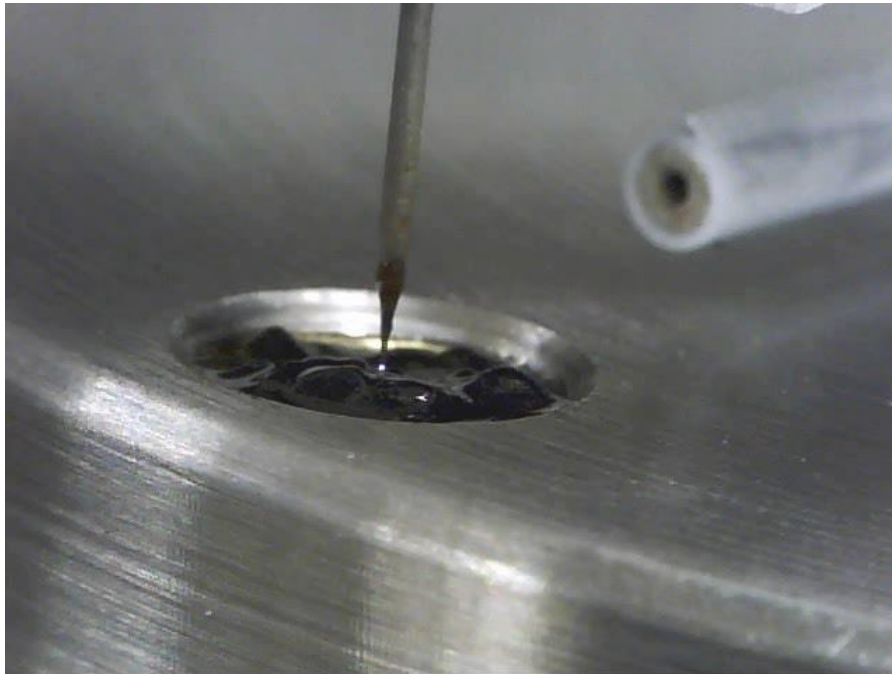
J. Chem. Phys. 2012, 136, No. 134307.

IL Monoprop Ignition

- Investigate the catalytic reactivity of ionic liquids via nanotip ambient ionization mass spectrometry (NAIMS).
- Experiments can be performed *on the benchtop*.
- High resolution and MS/MS.



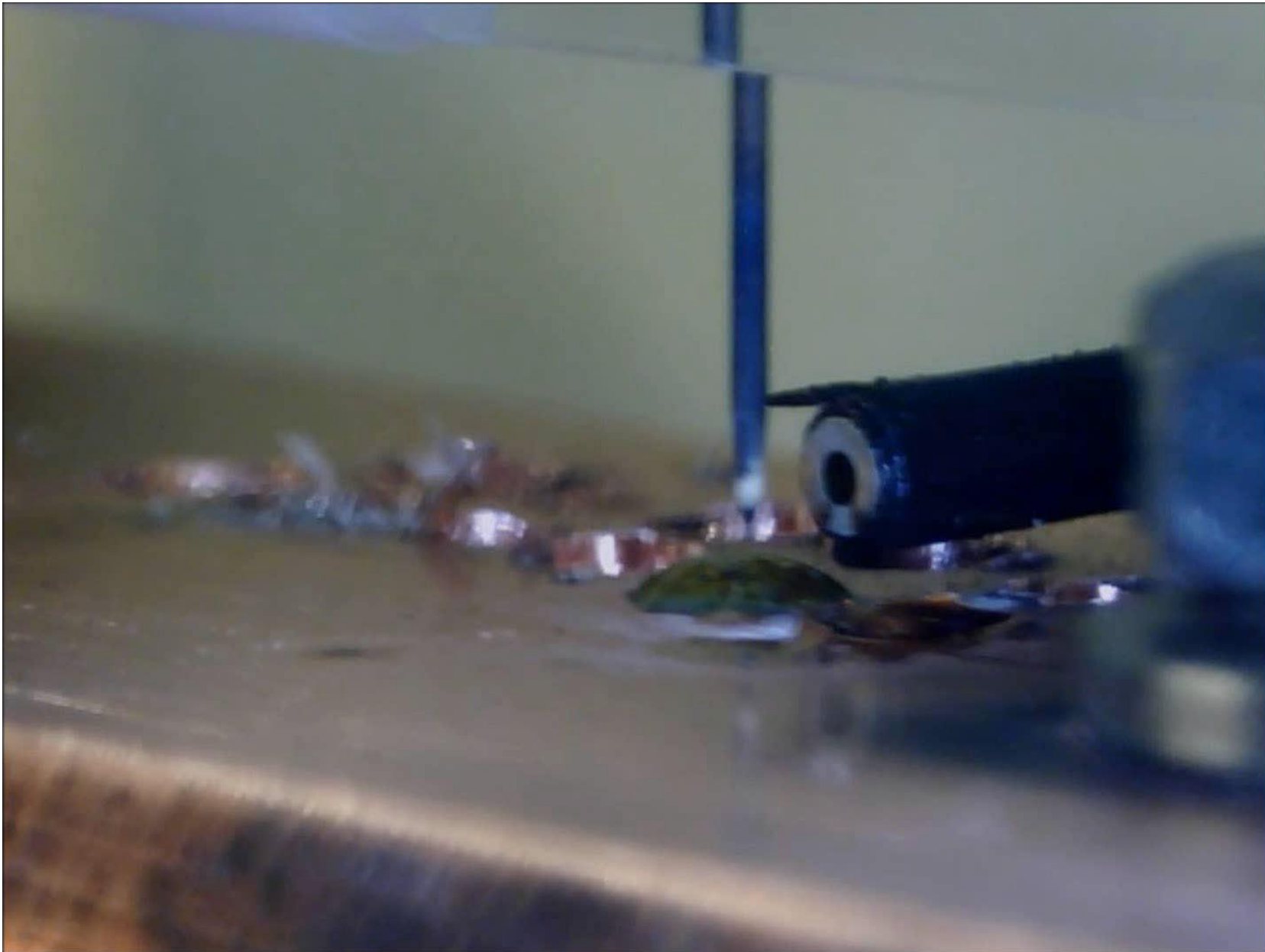
NAIMS Analysis



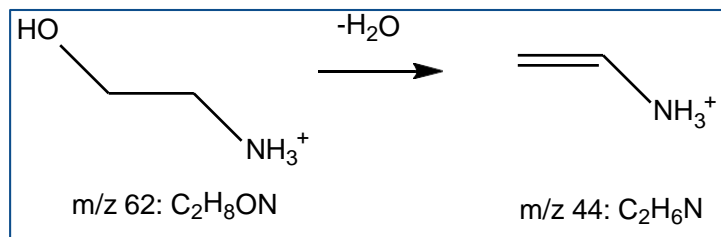
HEHN on S405 granules room temperature



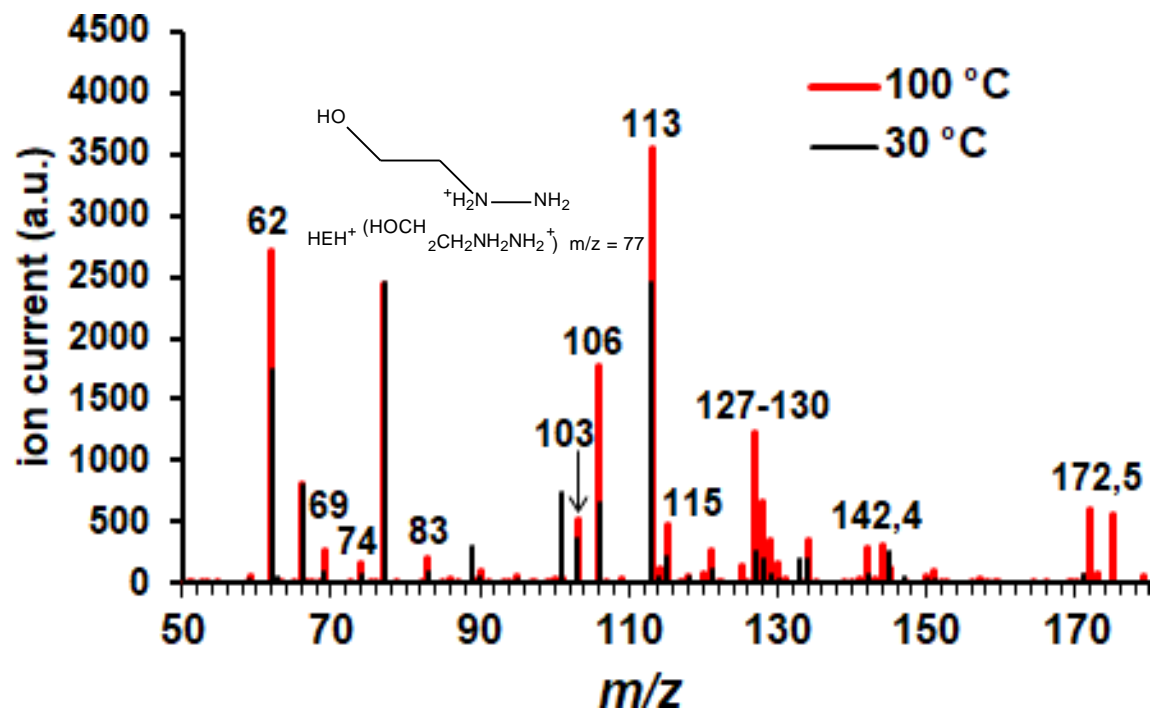
HEHN on S405 granules 50°C

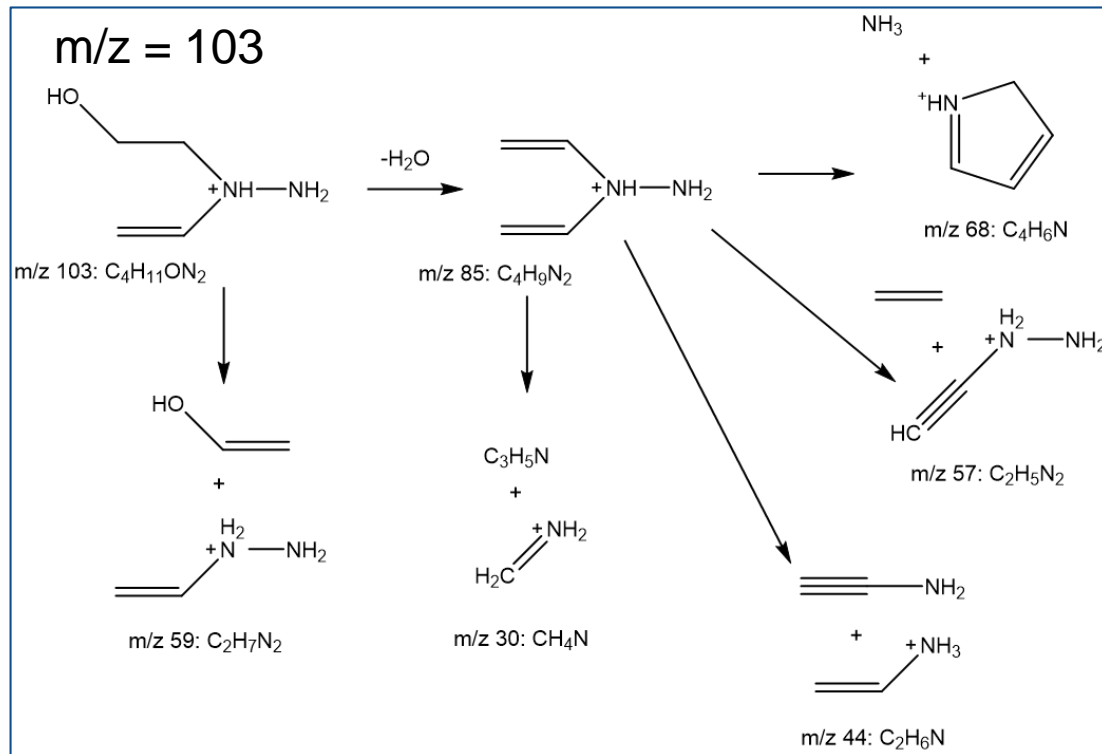


NAIMS Results

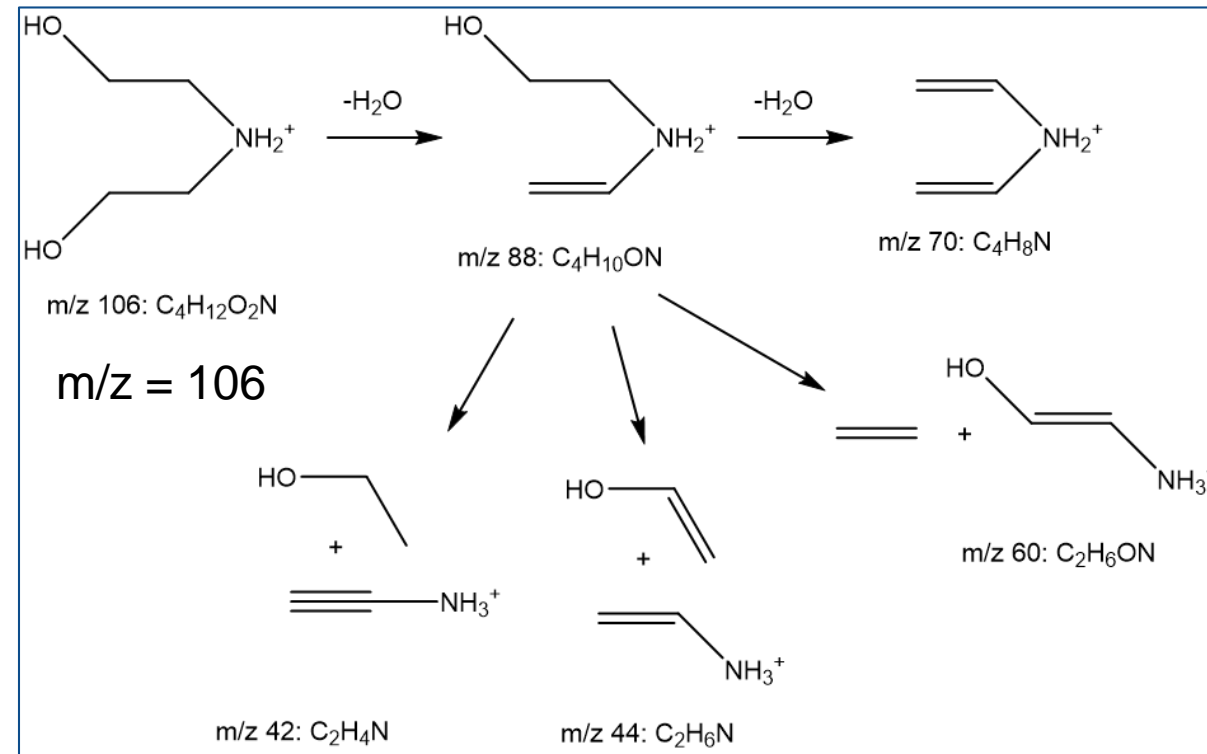


m/z = 62

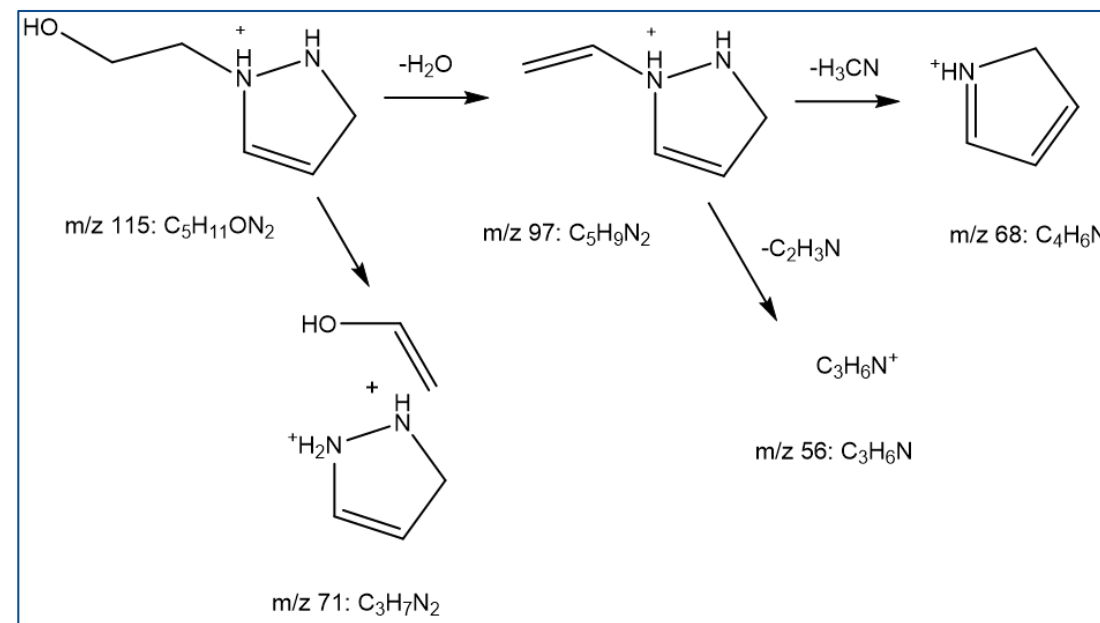
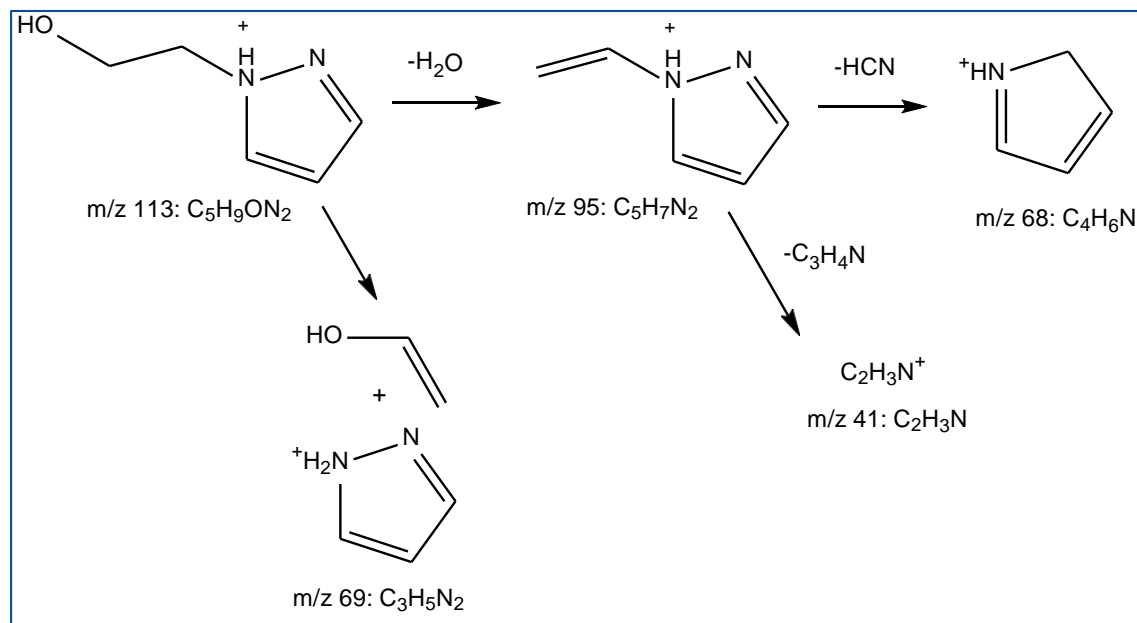




Possible structure and CID fragmentation pathways for m/z 103.0864 ($C_4H_{11}ON_2$)



CID fragmentation patterns and possible chemical structures for masses 106.08604 ($C_4H_{12}O_2N$) detected from NAIMS of HEHN on Ir catalyst at 100 °C.

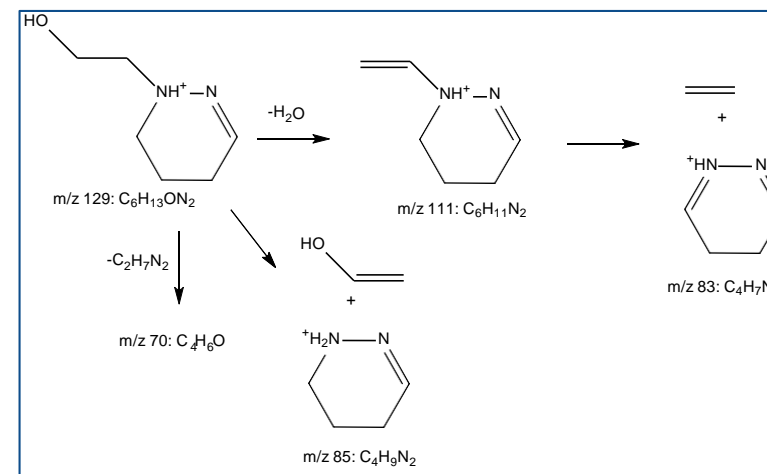
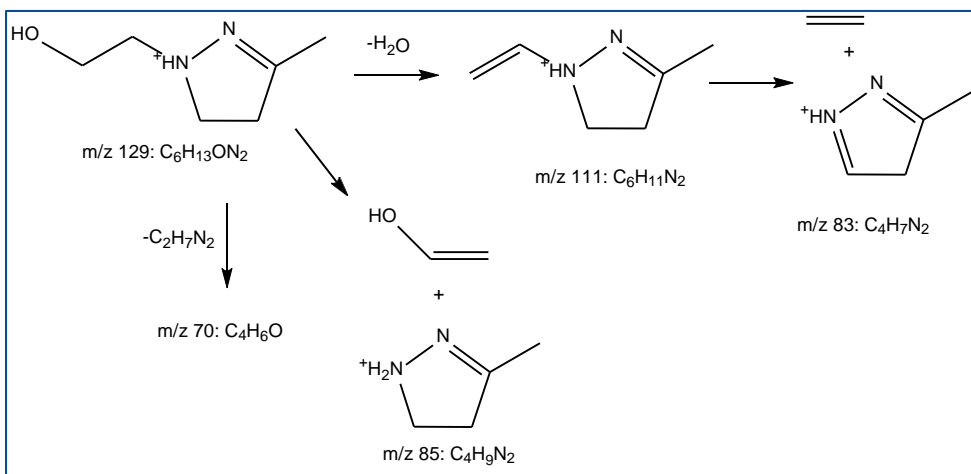
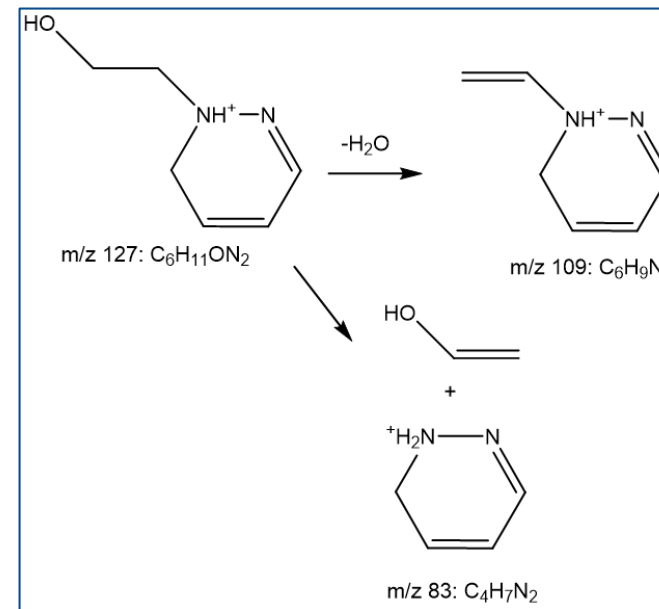
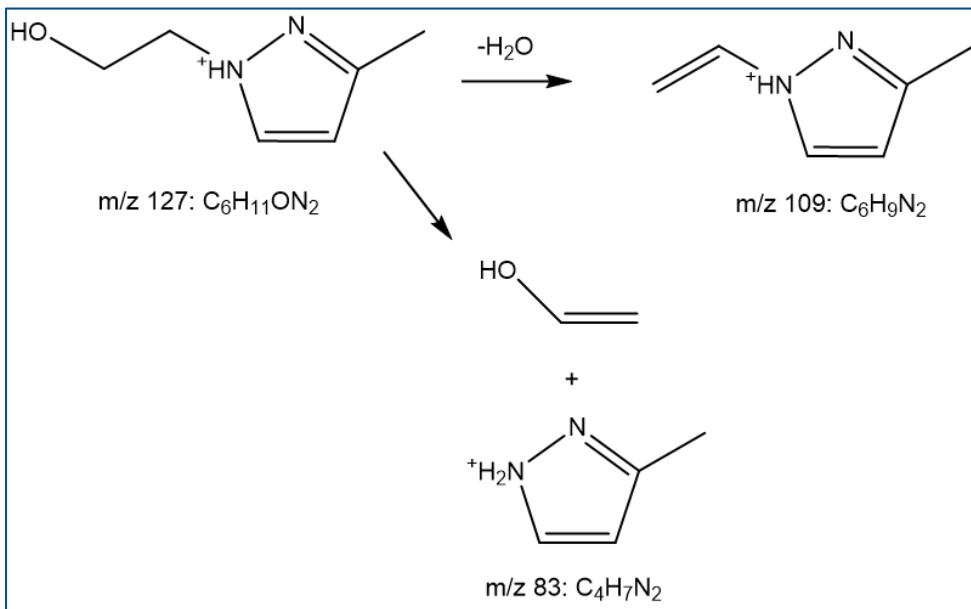


Proposed structures of m/z 113.0707 (C₅H₉ON₂) (left) and m/z 115.0864 (C₅H₁₁ON₂) (right) HEHN catalytic decomposition products and their CID fragmentation pathways.

J. Phys. Chem. Lett. 2022

DOI: 10.1021/acs.jpca.1c07408

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Proposed structures of m/z 127.0864 ($C_6H_{11}ON_2$) (top) and m/z 129.1020 ($C_6H_{13}ON_2$) (bottom) HEHN catalytic decomposition products and their fragmentation pathways.



Conclusions



Conclusions

- Catalytic reactivity of HEHN Ionic Liquid:
 - Proton transfer
 - NH_3 , propargyl, N_2O and ethanolamine formation
 - Surface recombinations to form larger hydrazines and cyclic structures
- Protic nature of ionic liquids can be very important to reactivity and physical properties.

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 - Oleg Kostko
 - Christine Koh
 - Amir Golan
- Zare Group (Stanford)

Mike Berman





Questions?