Mimic then Delineate Reaction Dynamics of Ionic Liquids in Spacecraft Electrospray Thrusters by Using Mass Spectrometry and Dynamics Simulations

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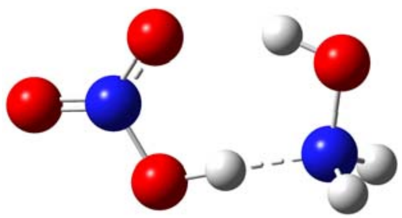
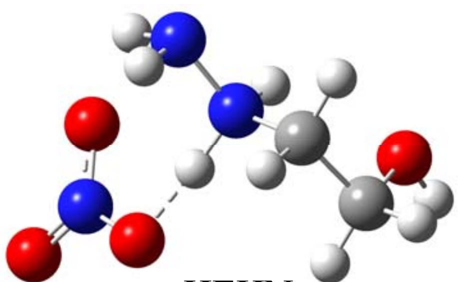
Hydroxylammonium nitrate (HAN)
2-Hydroxyethylhydrazinium nitrate (HEHN)



HAN

HAN and HEHN are the two task-specific IL initially developed for chemical propulsion by the Air Force Research Laboratory.

e.g. monopropellants consisting of chemicals that release energy through exothermic chemical decomposition.



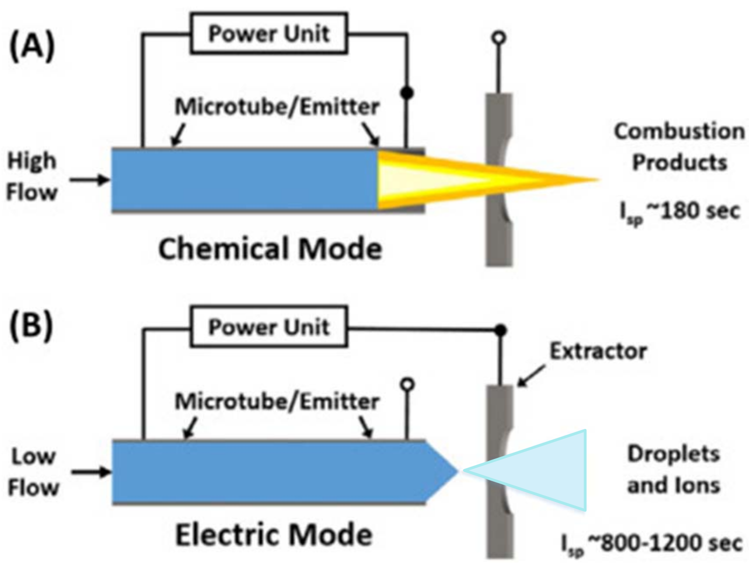
HEHN

Open the possibility of their applications in chemical-electric dual-mode propulsion systems due to:

- Inherent ionic nature
- High electrical conductivities
- Low viscosities

Dual-mode propulsion

operates with a single propellant in either a chemical or an electrospray mode.



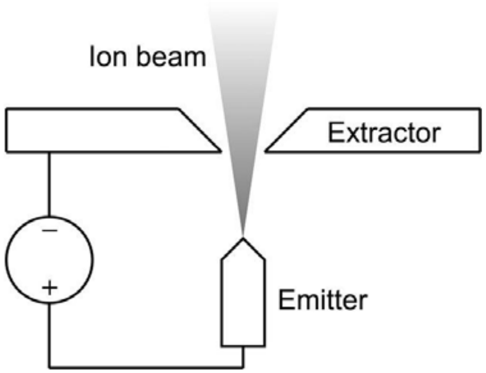
Advanced Spacecraft Energetic Non-toxic Propellant (ASCENT, formerly known as AF-M315E) is a mixture of HAN and HEHN.

- marks a major milestone in a national effort to develop new energetic propellants to be used in a dual-mode propulsion system.

Electrospray Thruster

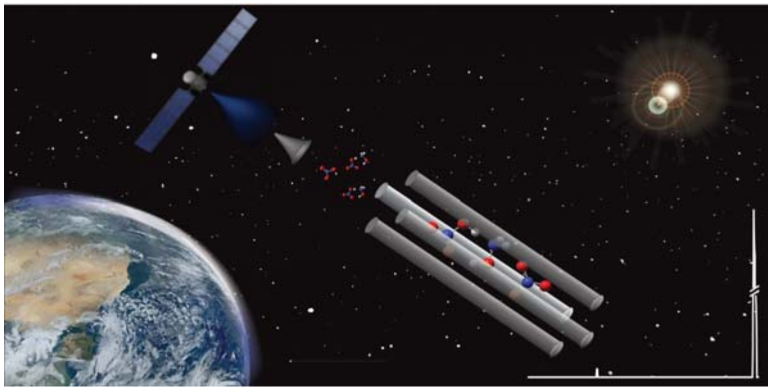
In an electrospray mode wherein charged IL clusters ions are emitted from a Taylor cone at the electrospray emitter tip

Accelerated through an E-field between the emitter and extractor to produce:



A thrust (F) proportional to $\sqrt{m_i(\text{ion mass})/z(\text{charge})}$

A specific impulse (I_{sp}) proportional to $\sqrt{z/m_i}$

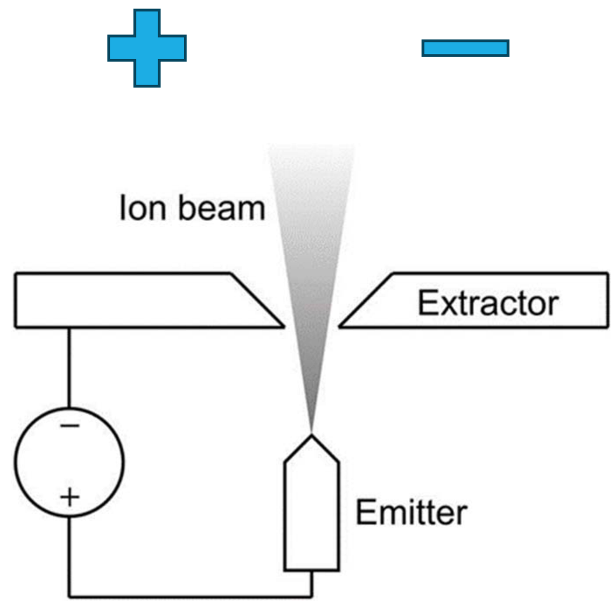


F. Mier-Hicks and P. C. Lozano, "Spacecraft-charging characteristics induced by the operation of electrospray thrusters" *J. Propul. Power* **33**, 456-467 (2017)

Electrosprays of Different Polarities

1) During electrospray, ions and clusters of a single polarity are extracted from IL. The remaining counterions are accumulated in the liquid.

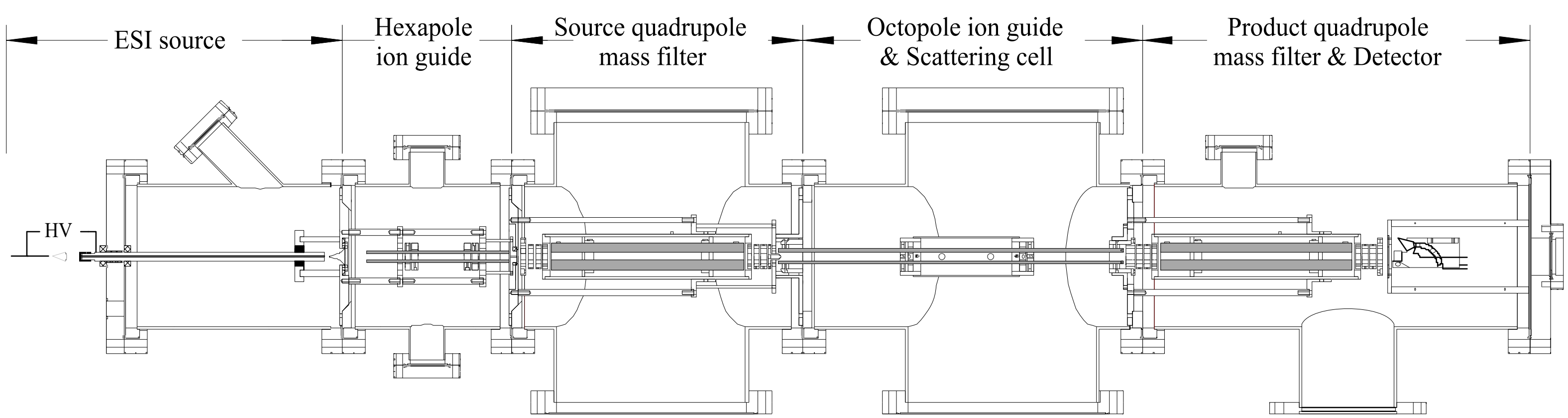
2) A fraction of product ions back-scatted and deposited on the surface of the spacecraft → surface charging induces electric disturbance to the spacecraft.



Investigations of Electrospray Using ESI-MS

ESI mass spectrometry closely mimics and thus represents a compelling avenue to explore electrospray thrusters in terms of

- ion emission
- injection into a vacuum
- ion-molecule reactions in space



Overview

Experimental:

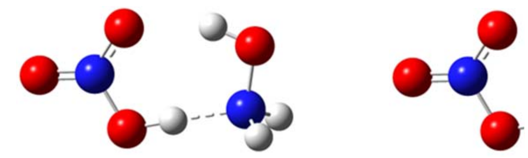
- Measurement of the electrospray ion plume compositions
- Collision induced dissociation of mass-selected cluster ions
- Using Monte Carlo simulation to mimic energy broadening in ion molecular reaction, incorporated into line-of-centers model to determine 0K dissociation threshold energy.

Theoretical:

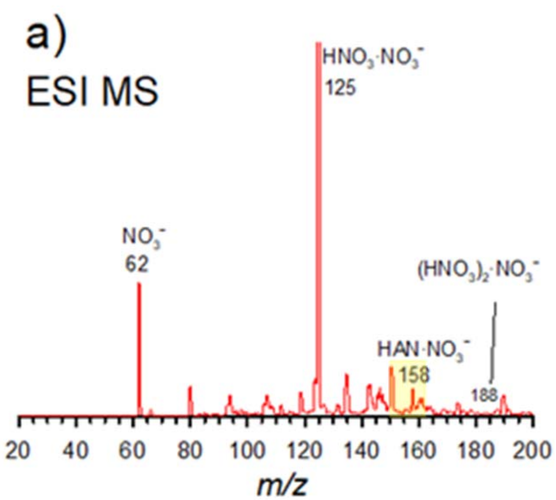
- Direct dynamics trajectory simulations
- Reaction coordinates and potential energy surface (PES)

Electrospray Performance of HAN

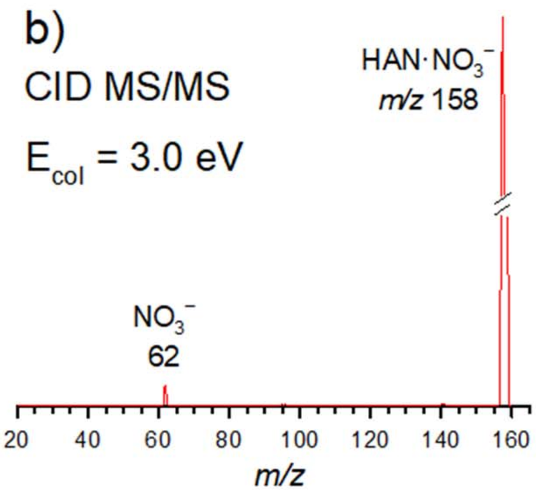
mass: 96 mass: 62



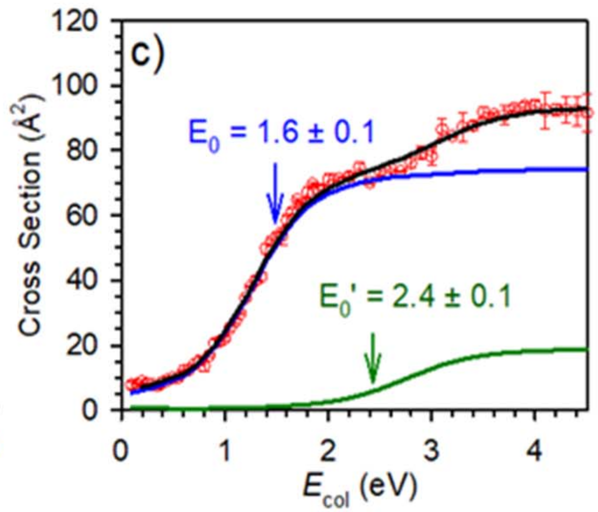
Negative ESI MS of HAN in 3:1 acetonitrile/water



CID product ion MS for HAN·NO_3^-



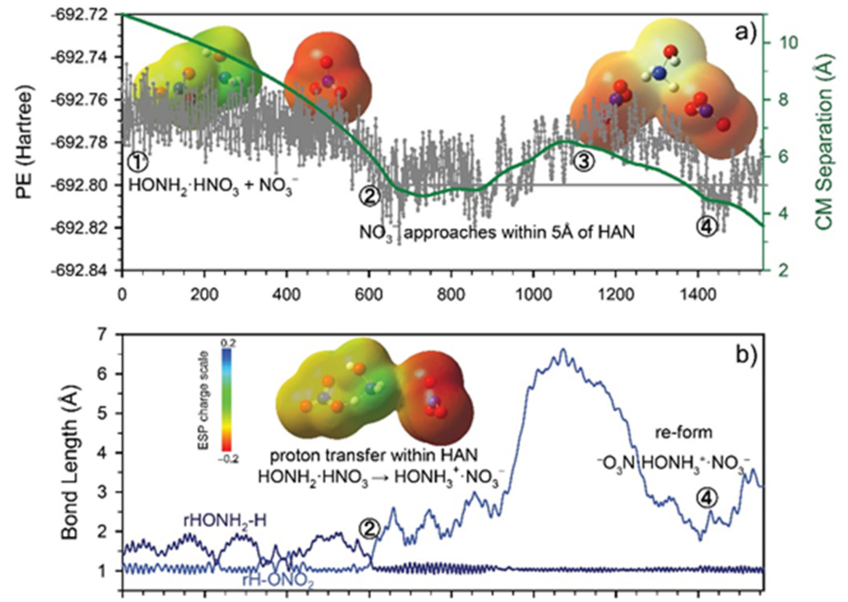
CID cross sections



PCCP, 2022, **24**, 14033 by Wenjing Zhou, J Liu*, Steven D. Chambreau, and Ghanshyam L. Vaghjiani

Recombination Trajectory of $HONH_2 \cdot HNO_3 + NO_3^-$

- The ionic HAN monomer (*i.e.*, $HONH_3^+ \cdot NO_3^-$) dominates in the solid phase, it converges to a covalent structure in the gas phase
- There were multiple proton transfer reactions between the $HONH_3^+$ and two NO_3
- The formation of $^-O_3N \cdot HONH_3^+ \cdot NO_3^-$ in Snapshot 2 and a brief proton transfer from $HONH_3^+$ to the incoming NO_3^- to form $O_3NH \cdot HONH_2 \cdot NO_3^-$



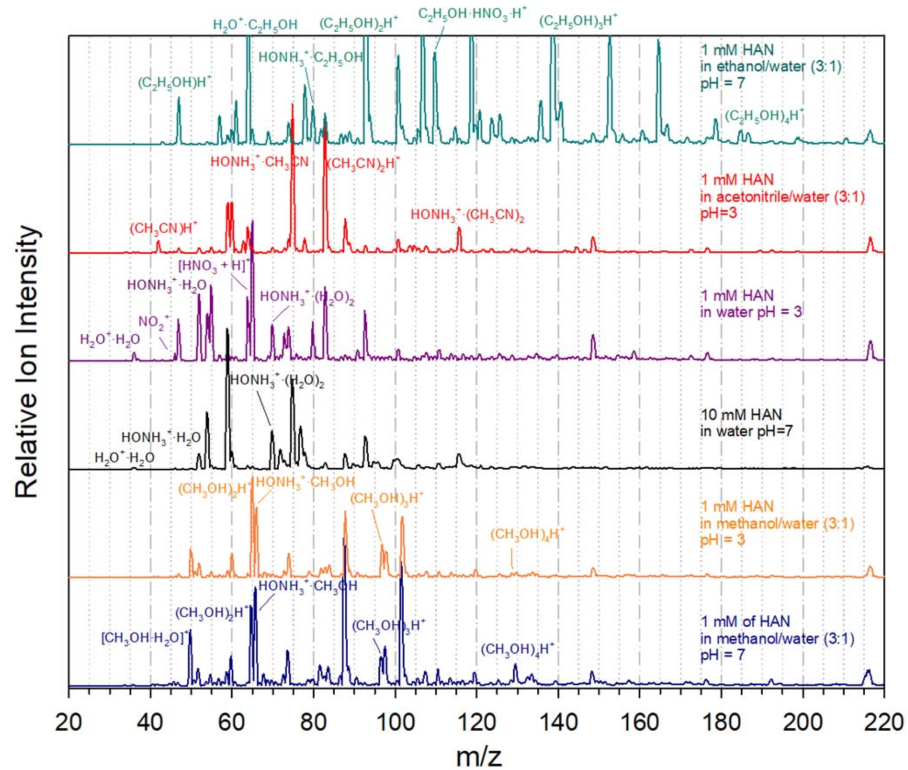
$$HAN \cdot NO_3^- \xrightarrow{Xe} [^-O_3N \cdot HONH_3^+ \cdot NO_3^-]^* \rightarrow HONH_2 \cdot HNO_3 + NO_3^- \qquad \Delta H = 1.55\ eV$$

$$HAN \cdot NO_3^- \xrightarrow{Xe} [O_3NH \cdot HONH_2 \cdot NO_3^-]^* \rightarrow HONH_2 + HNO_3 + NO_3^- \qquad \Delta H = 2.24\ eV$$

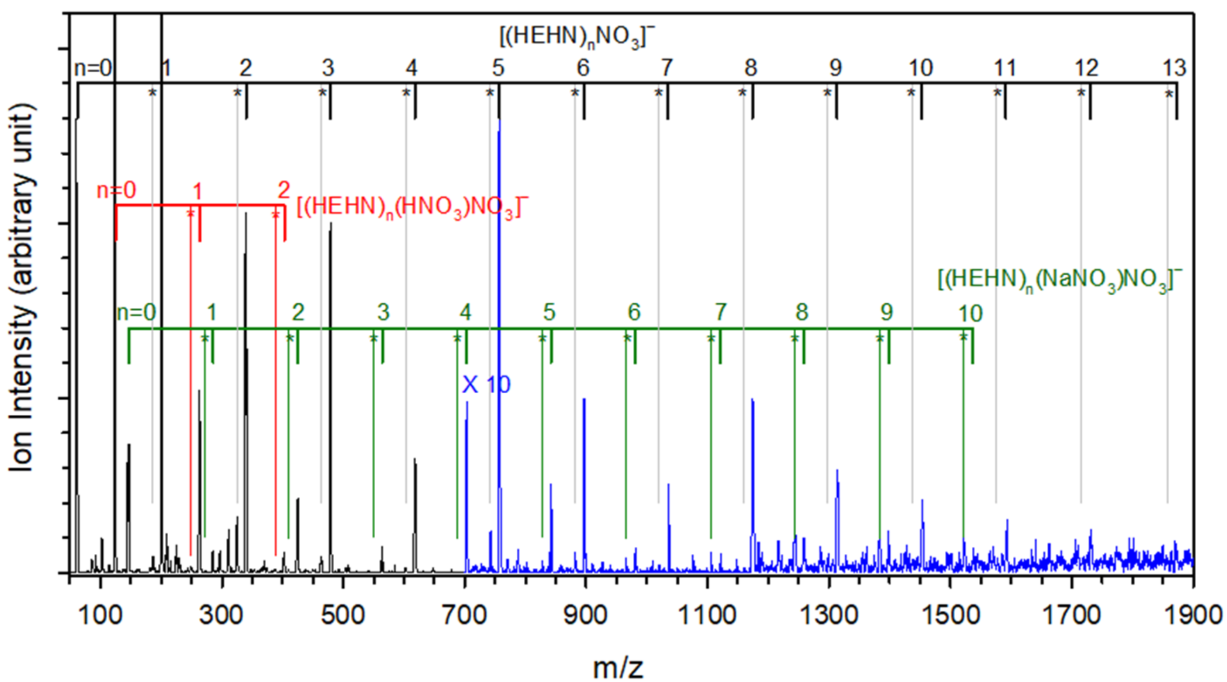
Positive ESI MS of HAN

In the collisions of H^+ + HAN, proton transfer occurred within the HAN species when H^+ was approaching within 8 Å of HAN, followed by

- $HONH_3^+ + HNO_3$
- $[H_2O + NH_2]^+ + HNO_3$
- $(HO)_2NO^+ + HONH_2$
- $H_2ONO_2^+$ to $NO_2^+ + H_2O$



Formation of HEHN Cluster Ions in Negative Electrospray



Most of the species can be grouped into three distinct series:

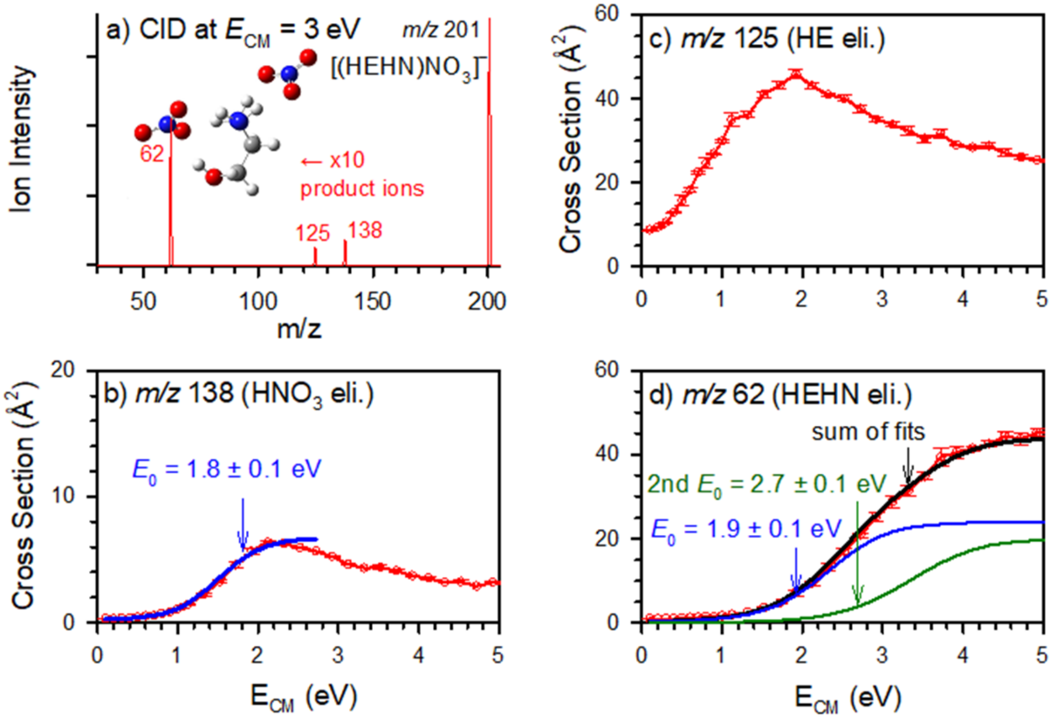
$[(HEHN)_nNO_3]^-$ (n = 0 – 13)

$[(HEHN)_n(HNO_3)NO_3]^-$ (n = 0 – 2)

$[(HEHN)_n(NaNO_3)NO_3]^-$ (n = 0 – 10).

Wenjing Zhou, J Liu*, Steven D. Chambreau, and Ghanshyam L. Vaghjiani, “Dynamics and thermochemistry of the negatively charged clusters in the 2-hydroxyethylhydrazinium nitrate ionic liquid system”, Phys. Chem. Chem. Phys., 2024, 26, 21697-21711. DOI: 10.1039/D4CP02329C.

Fragmentation of $[(HEHN)NO_3]^-$



$[(HEHN)NO_3]^-$

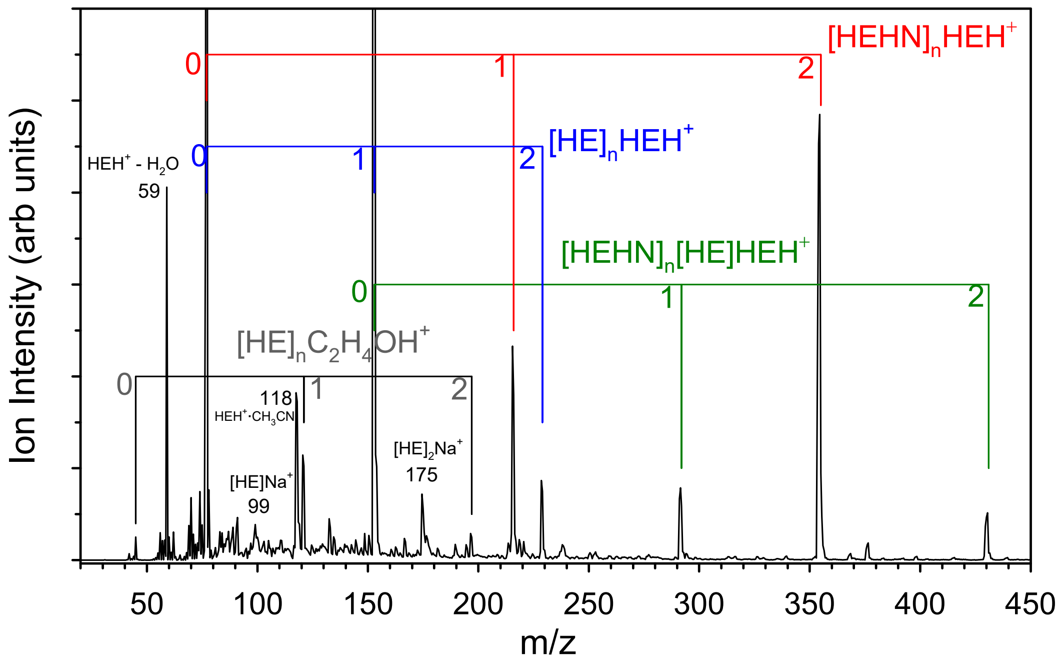
→ $[(HE)NO_3]^-$ + HNO_3 ΔH (0 K) = 1.63 eV

→ $[(HNO_3)NO_3]^-$ + HE ΔH (0 K) = 1.20 eV

→ NO_3^- + HEHN ΔH (0 K) = 1.80 eV

→ NO_3^- + HE + HNO_3 ΔH (0 K) = 2.59 eV

Formation of HEHN Cluster Ions in Positive Electrospray



The species in the ion plume can be grouped into four series:

$[HE]_nHEH^+$,

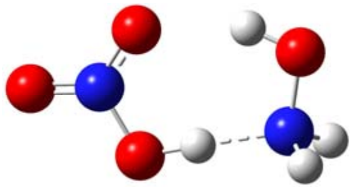
$[HE]_nC_2H_4OH^+$,

$[HEHN]_nHEH^+$, and

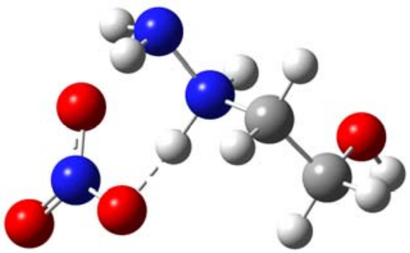
$[HEHN]_n[HE]HEH^+$ ($n = 0 – 2$).

W. Zhou, J Liu*, S. D. Chambreau, and G. L. Vaghjiani, "Formation and fragmentation of 2-hydroxyethylhydrazinium nitrate (HEHN) cluster ions: A combined electrospray ionization mass spectrometry, molecular dynamics and reaction potential surface study", *Phys. Chem. Chem. Phys.*, 2023, **25**, 17370-17384

HAN vs. HEHN



HAN



HEHN

- HAN undergoes intramolecular PT. No positively charged intact species.
- A variety series of cluster ions can be formed in both negative and positive electrospray of HEHN.
- To assess the utility of HAN and HEHN in ES thrusters, studies on efficiency parameters are needed, which are ongoing at the Air Force Research Laboratory.

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