Electrospray Ionization Tandem Mass Spectrometry and Molecular Dynamics Simulations of Hydroxylammonium Nitrate

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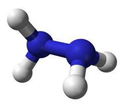
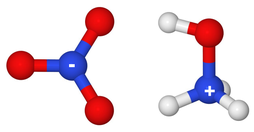
AFRL is Developing Ionic Liquids (ILs) as Green In-Space Propellants to Replace the Highly Toxic, Hydrazine Fuel

Traditional Fuel: Hydrazine

Next Generation IL Ingredient: Hydroxylammonium Nitrate (HAN)

Key:
H = O = N = S = C = F =

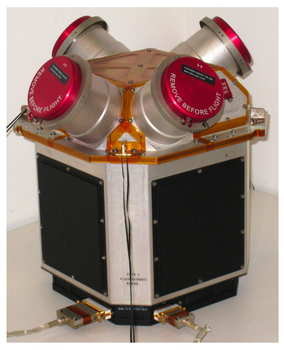




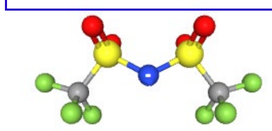
For Electrospray (ES) Thrusters? Yes, But Need More Studies

In ES Thrusters, Knowing Propellant Utilization & Electrical Efficiency are Important for Mission Planning

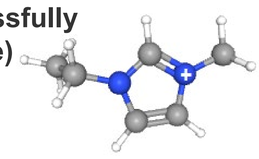
NASA's 2015 LISA Pathfinder Mission

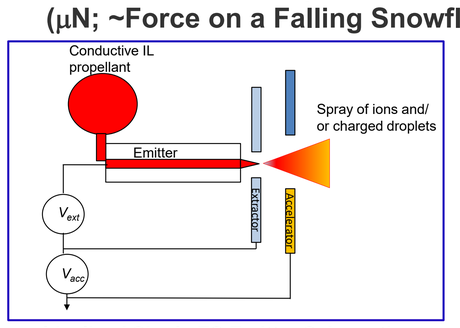


IL-based Thruster Can be a Key Technology Enabler



IL Precision Thrusters Operated Successfully (μN; ~Force on a Falling Snowflake)





Idealized Single ES Emitter Schematic

$n_e = (I_b V_b)/(I_b V_b + P_o)$

$n_m = (I_b M)/(Z \dot{m}_p^{\circ})$

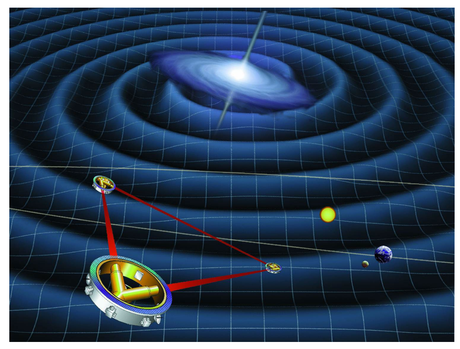
$T = (2M/Z)^{1/2} I_b (V_b)^{1/2}$

$I_{sp} = T/\dot{m}_p^{\circ} g$

Idealized Performance for Singular-type Ion Emission

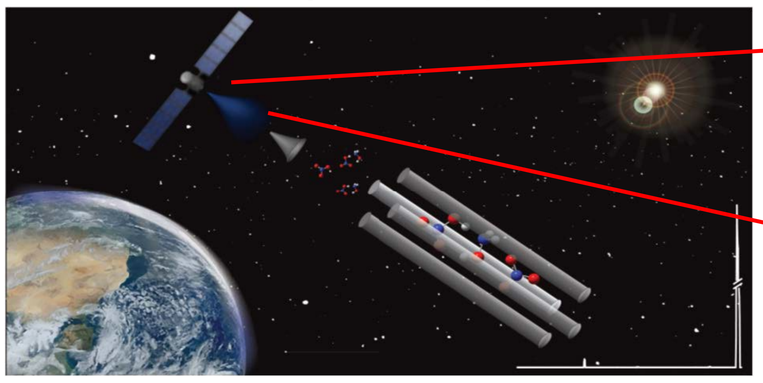
Key:
- n_e = electrical efficiency
- n_m = *mass utilization efficiency*
- T = thrust due to ion
- I_{sp} = *specific impulse*
- M = ion mass
- Z = ion charge
- I_b = thruster beam current
- V_b = net accelerator voltage
- P_o = power to create ion beam
- $\dot{m}_p^{\circ}$ = propellant flow rate
- g = acceleration due to gravity

Future (mid-2030s) Concept for Observation of Gravitational Waves

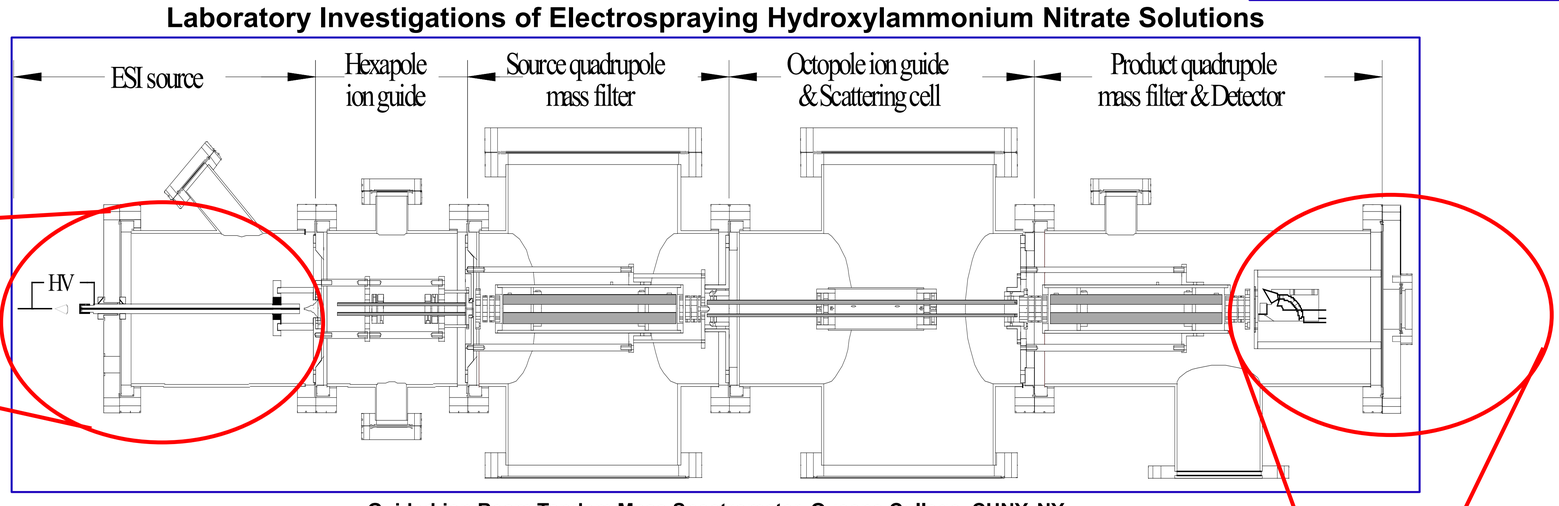


Laser Interferometer Space Antenna (0.01 nm Displacement Detection Capability)

Electrospray Ionization (ESI) Source of Mass Spectrometer Closely Mimics IL Electrospray Thrusters in Terms of Ion Emission and Injection into Space Vacuum

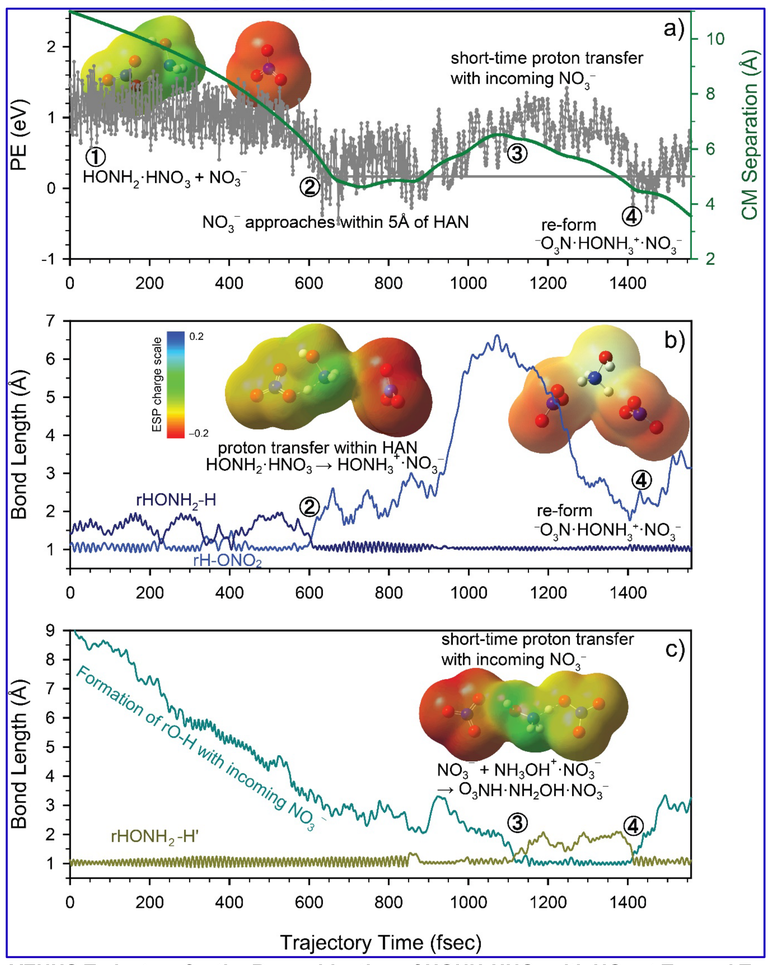


Laboratory Investigations of Electrospraying Hydroxylammonium Nitrate Solutions



Guided-ion Beam Tandem Mass Spectrometer, Queens College, CUNY, NY

MD Simulations of *m/z* = -158



VENUS Trajectory for the Recombination of $HONH_2HNO_3$ with NO_3^- at T_{vib} and T_{rot} = 300 K, ET = 0.05 eV and b = 0.0 Å, Calculated at the ωB97XD/6-31+G(d,p) Level of Theory

CID Spectrum of *m/z* = -158 Best Explained by a 2-channel Dissociation Mechanism

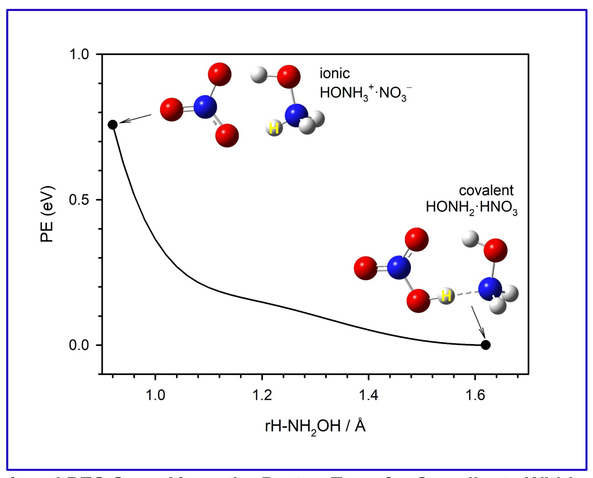
$$HAN \cdot NO_3^- \xrightarrow{Xe} [^-O_3N \cdot HONH_3^+ \cdot NO_3^-]^* \rightarrow HONH_2 \cdot HNO_3 + NO_3^- \quad \Delta H = 1.55\ eV$$

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

Line-of-centers Model-based Fitting of Cross Section for *m/z* = -158

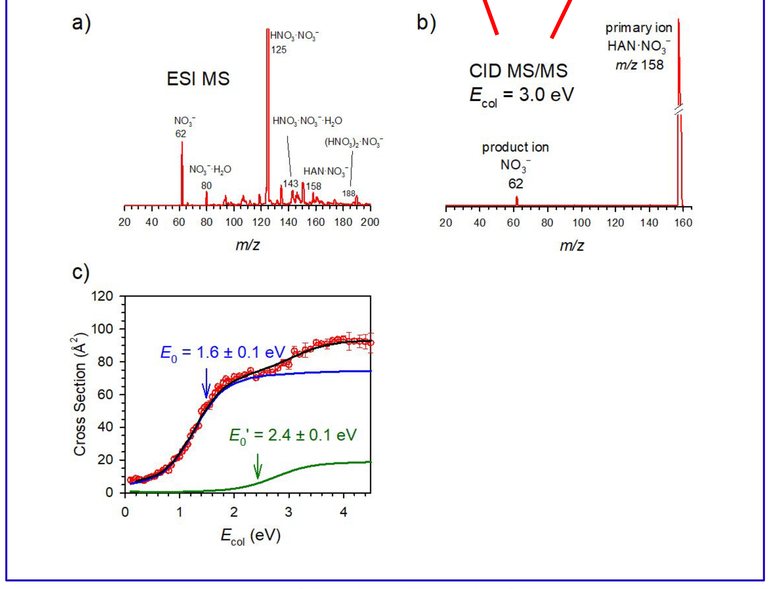
$$\sigma(E_{col}) = \sigma_0 \frac{(E_{col} + E_{vib} + E_{rot} - E_0)^n}{E_{col}}$$

Gas-phase HAN is Neutral



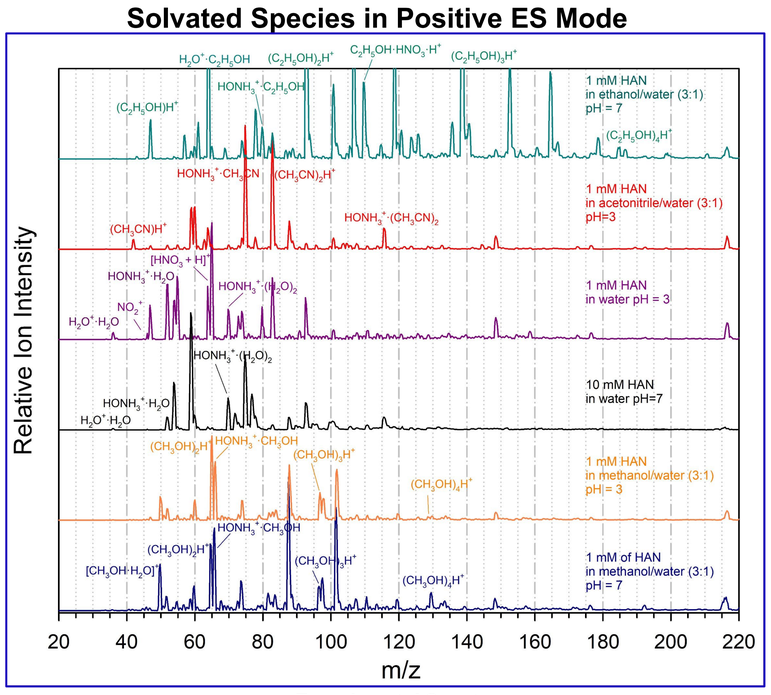
Relaxed PES Scan Along the Proton Transfer Coordinate Within $HONH_2 \cdot HNO_3$, Calculated at the ωB97XD/6-31+G(d,p) Level of Theory

HAN Species in Negative ES Mode



Experimental Spectra & Theoretical Fitting

Solvated Species in Positive ES Mode



Experimental Spectra

Conclusions:

- ES of HAN IL produces a variety of ions, which is mode dependent
- The nature, structure, & stability of these ions can be revealed by CID, QC, & MDS studies; here have we reported the details on *m/z* = -158
- To assess the utility of HAN IL in ES thrusters, studies on efficiency parameters are needed, which are ongoing at the Air Force Research Laboratory

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Further Readings at:

(1) Phys. Chem. Chem. Phys., 2022, *24*, 14033-14043 https://doi.org/10.1039/D2CP01571D
(2) J. Prop. Power, 2021, *37*, 650-659 https://doi.org/10.2514/1.B38160