Formation and Fragmentation of Ionic Liquid Cluster Ions Using ESI Mass Spectrometry, Dynamics Simulations and Electronic Structure Calculations

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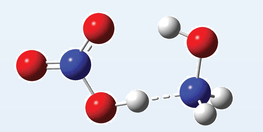
Introduction

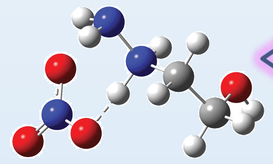
Ionic liquids (ILs) are chosen as green alternatives to the current, but toxic, volatile and sensitive monopropellant hydrazine owing to their reduced toxicity and improved performance.

Hydroxylammonium nitrate (HAN) and 2-hydroxyethylhydrazinium nitrate (HEHN) are the two task-specific ILs developed by the Air Force Research Laboratory. They can enhance mission performance on the basis of their applications in a dual-mode spacecraft propulsion system, which operates with a single propellant in either a chemical or an electrospray mode.

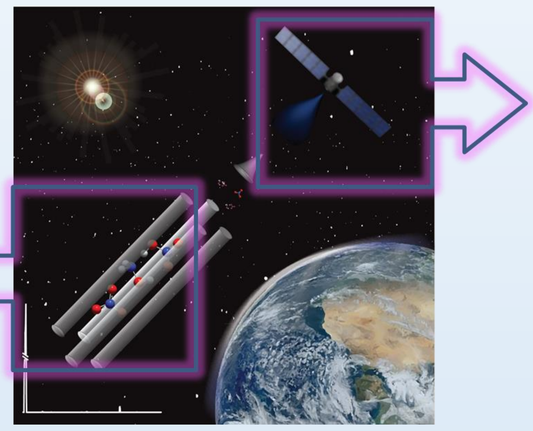
In an electrospray thruster, ions are accumulated in a Taylor cone and emitted to the gas phase in a high electric field (in either a droplet mode, an purely ionic mode, or a mixing of the two modes), from which the ionic species gain a large amount of momentum — A process that can be mimicked using electrospray ionization (ESI) mass spectrometry.

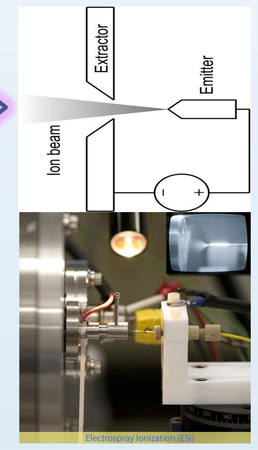


Hydroxylammonium nitrate (HAN)



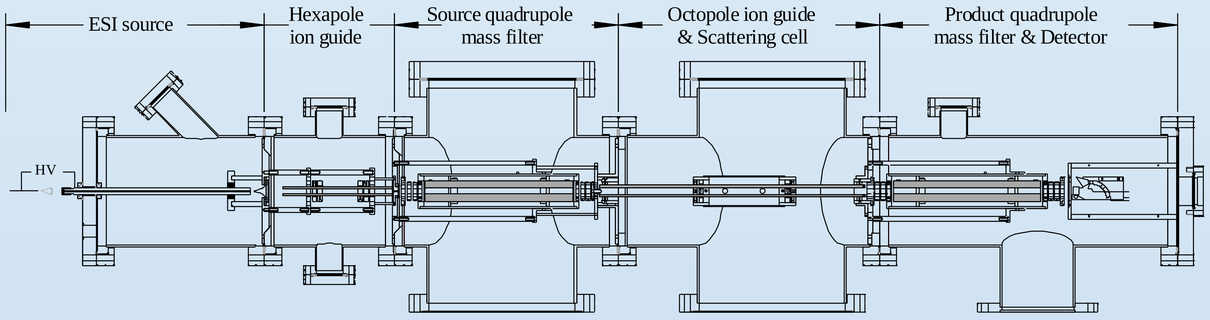
2-Hydroxyethylhydrazinium nitrate (HEHN)





Instrumentation, Experiment and Computation

Formation and CID of IL cluster ions using a ESI guided-ion beam tandem mass spectrometer



Computational modeling

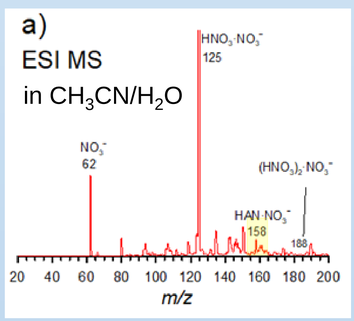
Direct dynamics trajectory simulations (based on Hase's VENUS code) were utilized to explore stable structures in the conformational landscape, and their individual reaction pathways and products under specific conditions.

Reaction coordinates and potential energy surface (PES) were mapped out for the most probable reaction products.

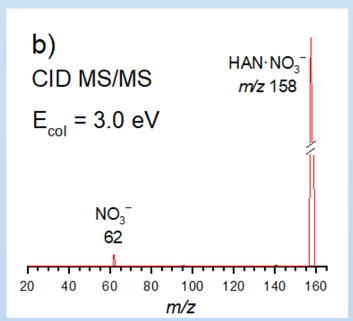
Theoretically-predicted IL cluster ion structures and reaction products were validated by comparing with ion-molecule experimental data.

Electrospray Performance of HAN and HEHN

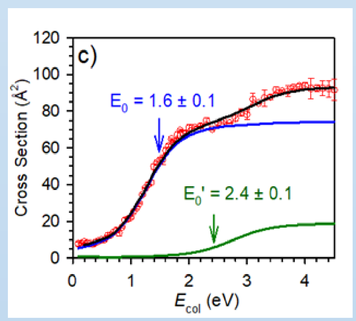
1. Structures of $HAN{\cdot}NO_3^-$ — the only cluster ion formed in negative electrospray of HAN



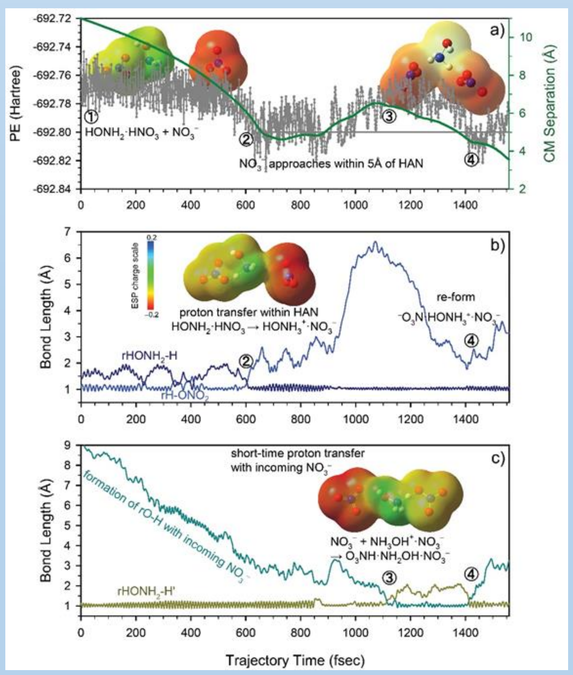
a) Negative ESI MS of HAN



b) CID product MS for $HAN{\cdot}NO_3^-$



c) CID cross sections of $HAN{\cdot}NO_3^-$ shows two pathways with a 4:1 ratio



📖 HAN exists in an ionic structure ($HONH_3^+{\cdot}NO_3^-$) in a solid phase, but converges to a covalent structure in the gas phase

Therefore, trajectories were set to mimic the recombination that may happen between a covalent HAN and a NO_3^- (snapshot ①) and the resulting cluster ion structure

In this representative trajectory, $^-O_3N{\cdot}HONH_3^+{\cdot}NO_3^-$ is formed (in snapshots ②–④) when NO_3^- is approaching HAN within 5 Å, followed by multiple intramolecular proton transfer (PT).

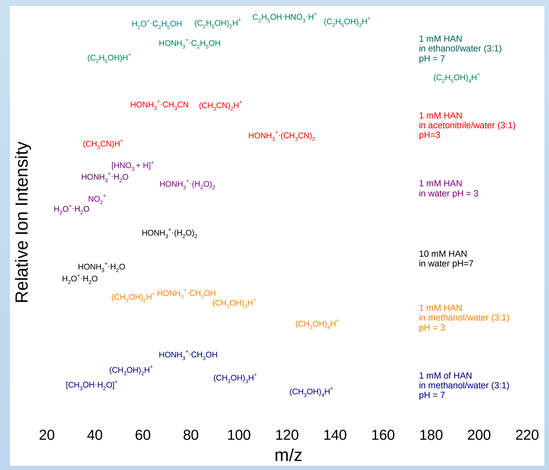
Trajectory results: **80%** of the collisions eventually converged to $^-O_3N{\cdot}HONH_3^+{\cdot}NO_3^-$, and only **20%** remained as $O_3NH{\cdot}HONH_2{\cdot}NO_3^-$ at the end of the trajectories.
The results support the two CID pathways in Fig c. Trajectory yields and calculated dissociation thresholds (below) matched experimental product branching ratio and E_0:

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

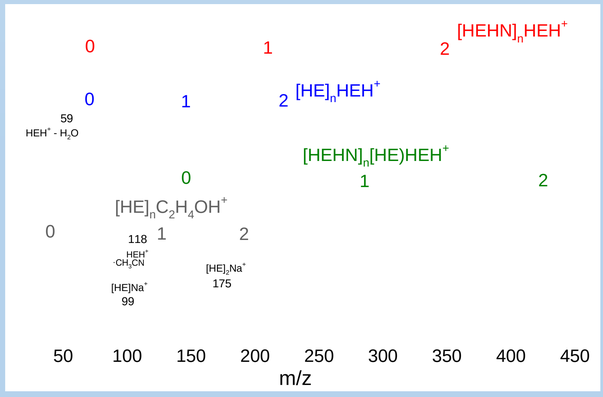
$$HAN{\cdot}NO_3^- \xrightarrow{Xe} [O_3NH{\cdot}HONH_2{\cdot}NO_3^-]^* \rightarrow HONH_2 + HNO_3 + NO_3^- \quad \Delta H = 2.24\ eV$$

2. Fate of $HAN + H^+$ in positive electrospray

- No HAN clusters formed in positive electrospray.
- Rationalization is provided by dynamics simulations of $HAN + H^+$, which revealed following consequences:
  a) attack of H^+ upon $-NH_2$ in the $HONH_2$ moiety to form separated $HONH_3^+ + HNO_3$;
  b) attack of H^+ upon the -OH in the $HONH_2$, forming three body products $[H_2O + NH_2]^+ + HNO_3$;
  c) collision of H^+ with and binding to HNO_3; meanwhile, the ensuing $(HO)_2NO^+$ transferred proton to $HONH_2$;
  d) attack of H^+ upon the -OH in HNO_3, followed by decomposition of $H_2ONO_2^+$ to $NO_2^+ + H_2O$



3. Formation and dissociation of cluster ions formed in positive electrospray of HEHN



cluster ions	ΔH (eV)	fragment ion	complementary neutral
HEH^+	0.18 (1.96*)	$[CH_3CH{=}NHNH_2]^+$	H_2O
$[HE]HEH^+$ (Structure I for *m/z* 153)	1.38	HEH^+	HE
$[CH_2CHHNH_2][NH_2NH_2CH_2CH_2OH]^+{\cdot}H_2O$ (Structure II for *m/z* 153)	0.54 1.49	$[CH_2CHHNH_2]{\cdot}[NH_2NH_2CH_2CH_2OH]^+$ $[HEH]^+$	H_2O $CH_2CHNHNH_2 + H_2O$
$[HE]_2HEH^+$	1.07	$[HE]{\cdot}HEH^+$	HE
$[HOCH_2CH_2NHNHCHCH_3]^+{\cdot}H_2O$ (first structure for *m/z* 121)	0.54	$[HOCH_2CH_2NHNHCHCH_3]^+$	H_2O
$[HOCH_2CH_2N(NH_2)CHCH_3]^+{\cdot}H_2O$ (another structure for *m/z* 121)	0.40	$[HOCH_2CH_2N(NH_2)CHCH_3]^+$	H_2O
$[HE][OHCH_2CH_2NHNHCHCH_3]^+{\cdot}H_2O$	1.61	$[HEH]^+$	$H_2O + OHCH_2CH_2NHNCHCH_3$
$[HEHN]HEH^+$	0.80 1.39	$[HE]HEH^+$ HEH^+	HNO_3 HEHN
$[HEHN]_2HEH^+$	2.53 3.12	$[HE]HEH^+$ HEH^+	HEHN, HNO_3 HEHN
$[HEHN][HE]HEH^+$	1.08 1.09	$[HEHN]HEH^+$ $[HE]HEH^+$	HE HEHN
$[HEHN]_2[HE]HEH^+$	1.19 2.93	$[HEHN]_2HEH^+$ $[HE]HEH^+$	HE HEHN

Conclusions

- ❖ HAN undergoes intramolecular PT in the presence of water, NO_3^-, H^+ or another HAN. ESI of HAN produces few negatively charged and no positively charged intact species.
- ❖ A variety series of cluster ions can be formed in positive electrospray of HEHN. All are prone to fragmentation: HEH^+ and $[HEHN]HEH^+$ represent the most common fragment ions while HE, HEHN and HNO_3 represents the complementary neutral fragments.
- ❖ Implications on electrospray thruster applications: fragmentation, specific impulse (I_{sp}), and autocatalytic neutral reactions in ion plume
- ❖ 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.

References
W. Zhou, J. Liu, S. D. Chambreau and G. L. Vaghjiani, *Phys. Chem. Chem. Phys.*, 2022, 24, 14033-14043 (HAN work)
W. Zhou, J. Liu, S. D. Chambreau and G. L. Vaghjiani, to be submitted, 2023 (HEHN work).

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