Synthesis of Cyanide Ions (CN^-) via Hypervelocity Impacts (HVIs)

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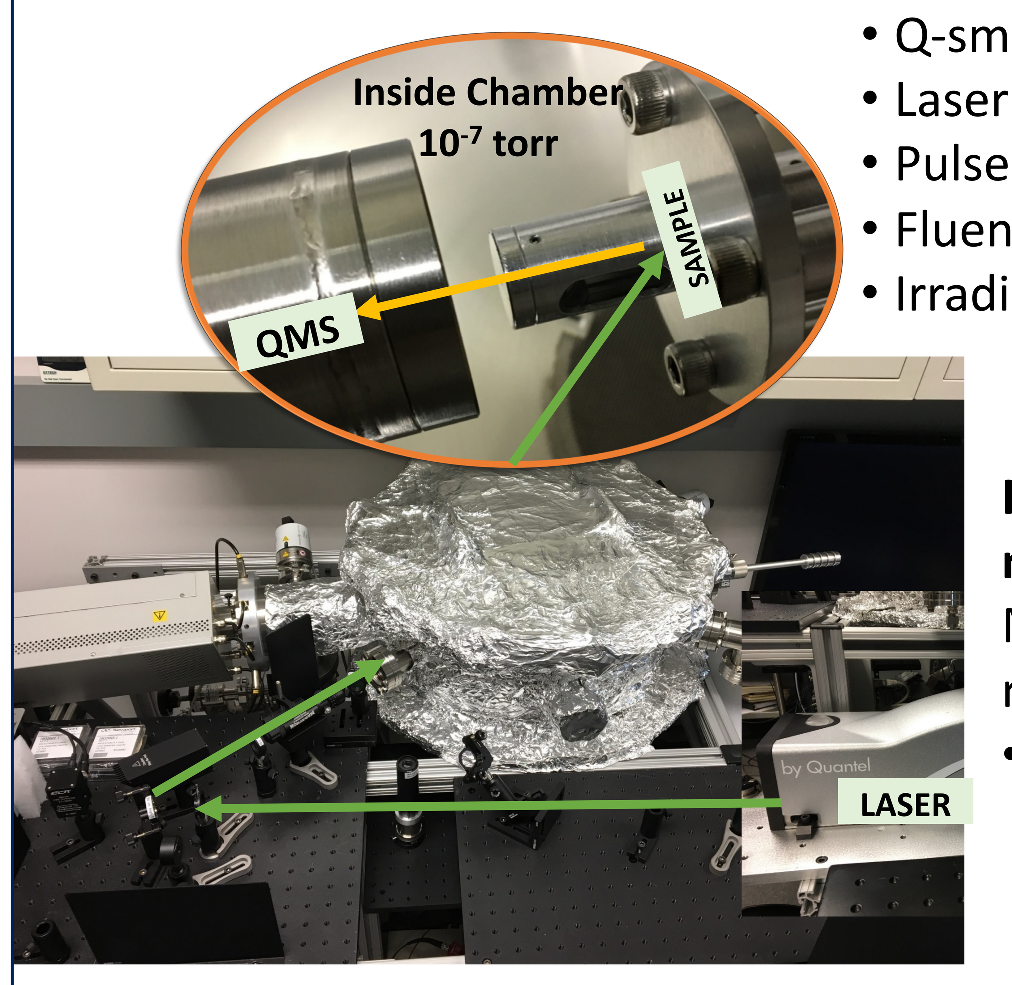
Introduction and Background

Hydrogen cyanide (HCN) is a particularly important prebiotic material that facilitates a variety of chemical reactions for organic synthesis (Saladino et al., 2012). Previous studies have demonstrated the synthesis of CN^- or cyano radicals via energetic reactions such as photon irradiation, electric discharge, UV radiation, and hypervelocity impacts (HVIs), using simple precursor compounds NH_3, CO, H_2O, N_2, graphite (Ferus et al., 2017; Sugita and Schultz, 2009). Researchers have suggested that exogenous infall may not just *deliver* organic materials to planetary surfaces (Chyba and Sagan, 1992), but also *enable* molecular rearrangement (via ionization and recombination) and synthesis of essential prebiotic compounds in the post-impact plasma plume (Managadze, 2003; Farcy et al., 2017). This study aims to carefully re-investigate, confirm, and quantify the synthesis of CN^- via HVIs in a vacuum (10^{-7} torr), in order to understand the effects of meteorite impacts on planetary bodies without substantial atmosphere, e.g., Ceres. We used high energy laser pulses (irradiance ≥ 3×10^8 W/cm²) to simulate extreme impact plasma recombination conditions in the laboratory. Carbonates and N-salts (ammonium and nitrate) are chosen because they are common inorganic sources of N and C on planetary surfaces that could dominate contribution to synthetic yields.

Objectives

1. Synthesis of CN^- using inorganic solids (carbonate and N-salts) via HVIs in vacuum (10^{-7} torr)
2. Investigate the effects of oxidation states of substrate (NO_3^- (N [+5]) and NH_4^+ (N [−3]) on yield of CN^-
3. Kinetic energy distribution of ions from laser ablation

Experimental Setup



Pulsed laser ablation (PLA)

- Q-smart 850 Laser, 1064 nm
- Laser energy: ≥ 30 mJ
- Pulse duration: 9 ns
- Fluence: > 2.8 J/cm²
- Irradiance: ≥ 3×10^8 W/cm²

Hiden Quadrupole mass analyzer

Measure mass to charge ratio (m/z) of ions

- Intensity of signal is proportional to concentration of ions

$$CaCO_3 + [NaNO_3 \text{ or } NH_4Cl] \rightarrow CN^-$$

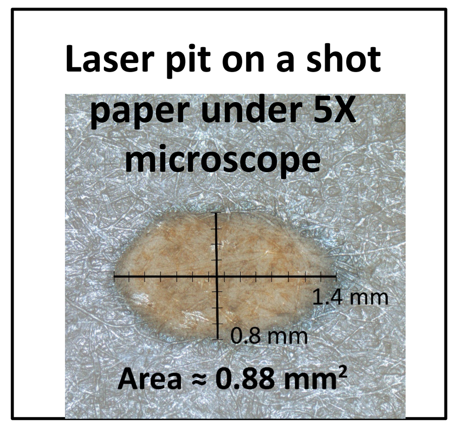
Preparation of 200 mg pellet mixture

- **C source:** $CaCO_3$ or $Ca^{13}CO_3$
- **N source:** $NaNO_3$ or $Na^{15}NO_3$; NH_4Cl or $^{15}NH_4Cl$

Heavier isotope labeled material

Expected mass shift from m/z 26 to 27, 28

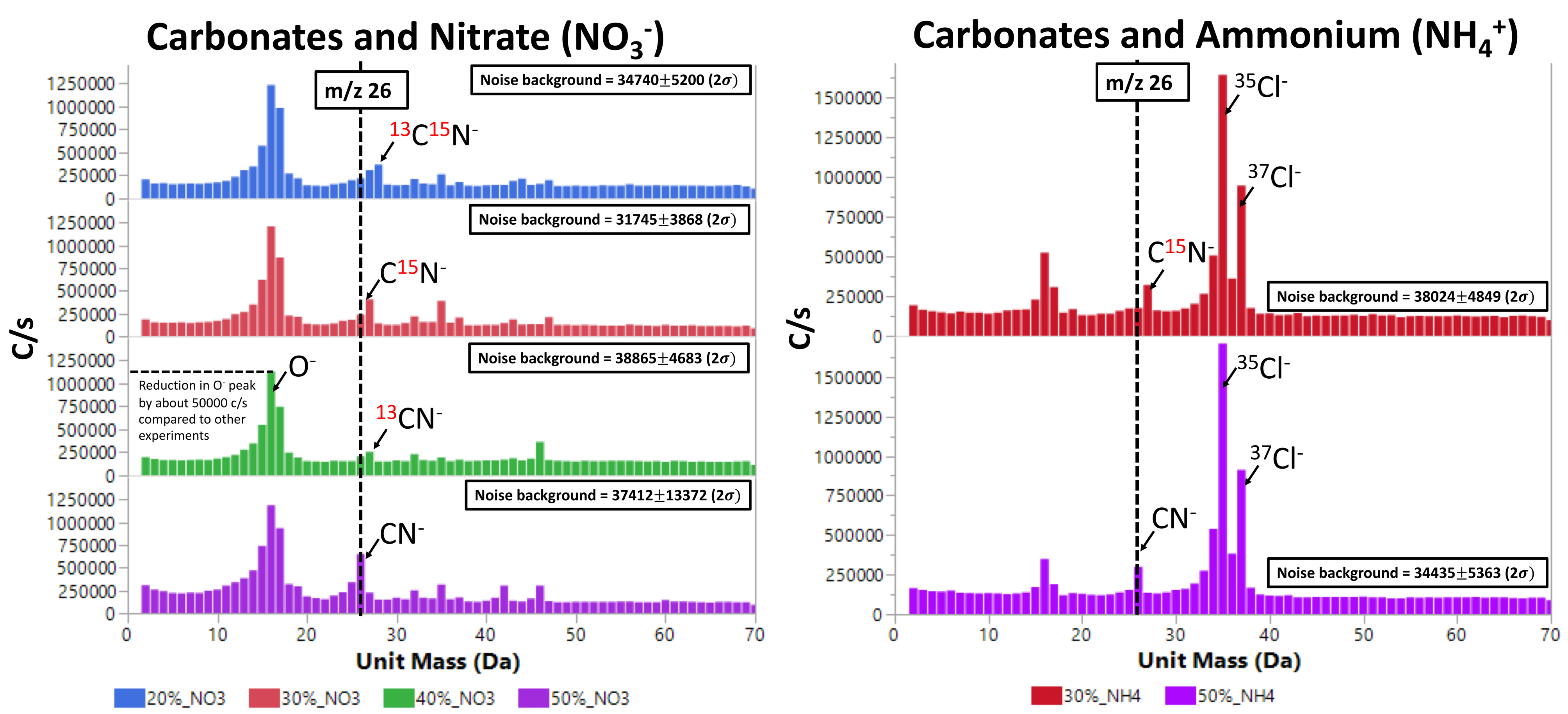
Laser pit on a shot paper under 5X microscope



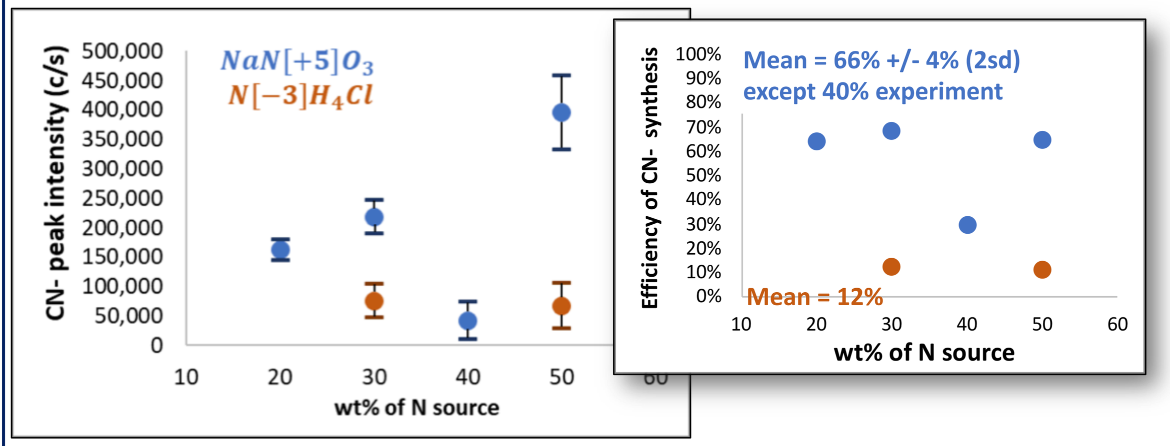
Experimental results

1. Synthesis of CN^- from both nitrate and ammonia salts.

[NOTE]: Each spectrum is a summation of 15 mass spectra that collected at ion energy from 1 eV to 15 eV.



2. Qualitative calibration curve as a function of concentration



[NOTE]: The CN^- peak intensity is the number of counts above limit of detection (LOD, calculated as $X_B + 3S_B$) at corresponding unit mass station. The error bar represents the uncertainty of LODs over 15 mass spectra at 2σ (95% CI).

[COMMENTS]: Unexpected low CN^- intensity at 40 wt% NO_3 experiment could be due to

1. **Off-center laser shot to the sample aperture**, resulting in a fraction of ions from plasma transmit into QMS. We have ~ 50000 c/s reduction at O^- peak.
2. **Insufficient atomization of N from NO_3^-**. We have ~45000 more c/s of NO_2^- at 40 wt% NO_3 experiment compared to its 50 wt% counterpart.
3. **instrumental instability**

Efficiency of CN^- synthesis using peak intensity (background subtracted):

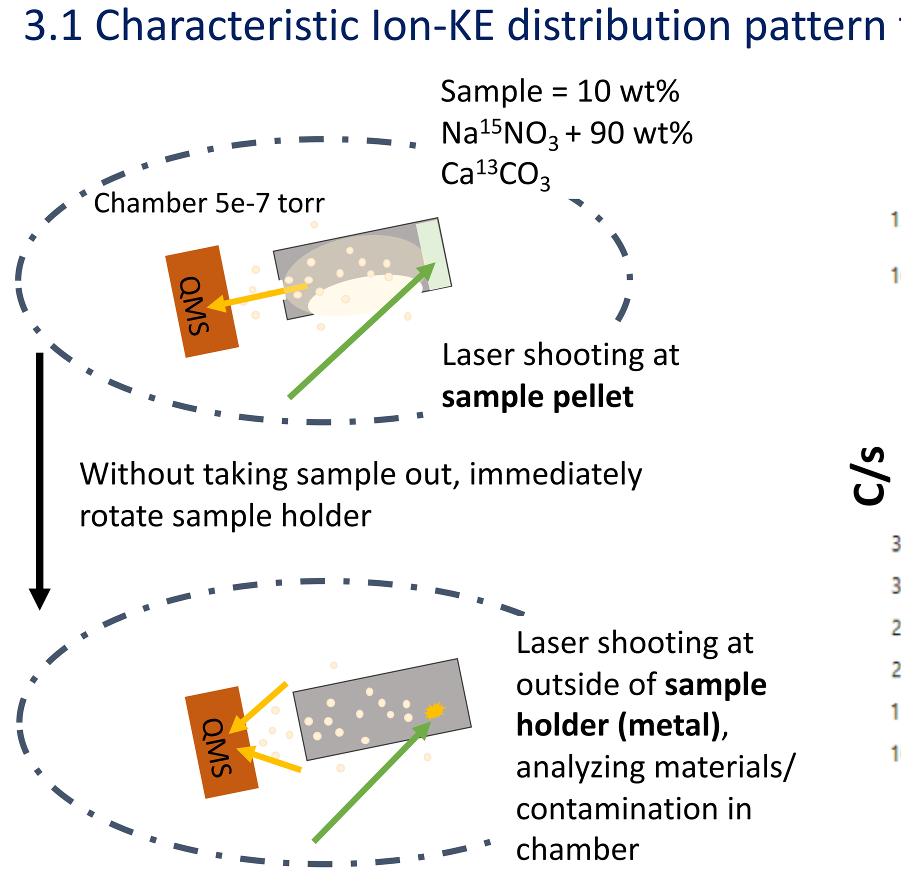
NH_4Cl: $CN^-/NH_4^- = CN^-/Cl^-$

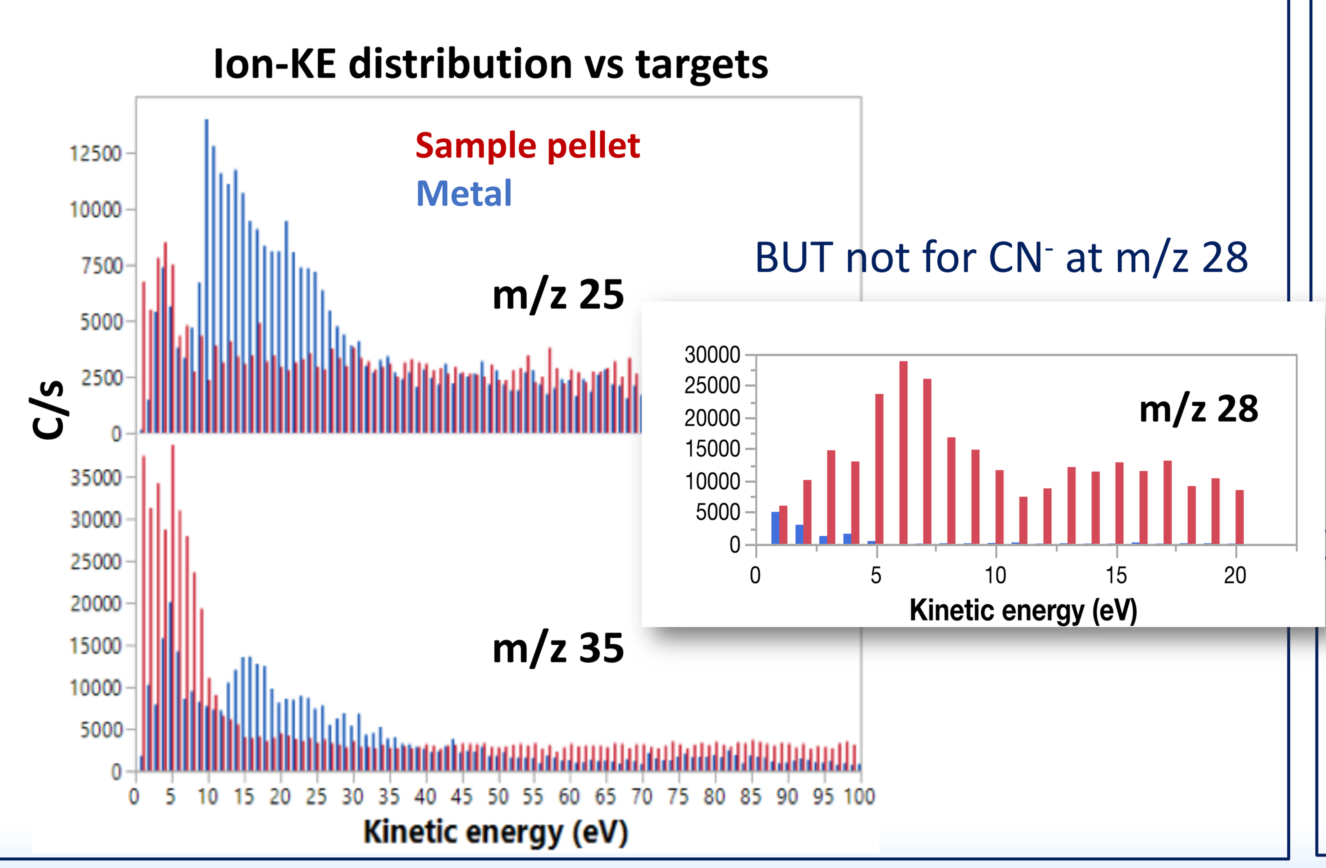
$NaNO_3$: $CN^-/NO_3^- = CN^-/(CN^- + CNO^- + NO_2^-)$

We only observed CN^-, CNO^-, NO_2^- in spectra from m/z 0 to 70 Da. We did not see observable peaks after 70 Da. We thus assume $NO_3^- \approx CN^- + CNO^- + NO_2^-$.

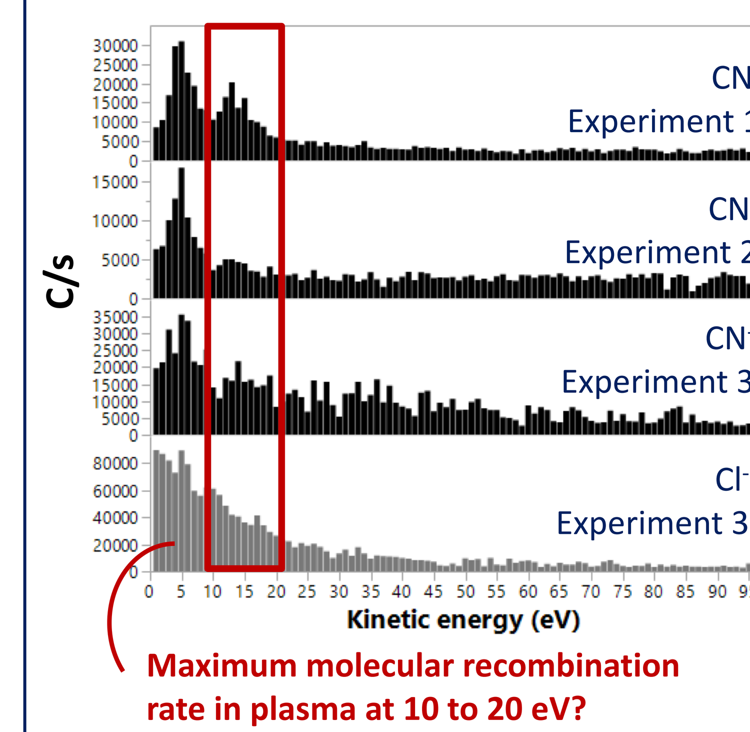
3. Distribution of ions as a function of kinetic energy (KE) from 1-100 eV

3.1 Characteristic Ion-KE distribution pattern for metal target: optimal KE energy from 10 to 35 eV ?





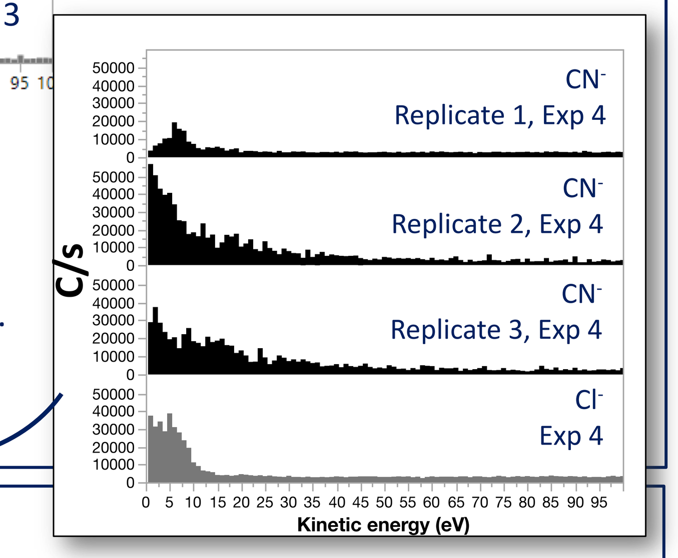
3.2 Characteristic Ion-KE distribution pattern for CN^- at 10-20 eV?



[NOTE]: Synthesis of CN^- from three separate experiments (1,2,3) using carbonate and ammonia salt sample mixture. All analyses were taken at the same date, same instrumental and laser parameters, pressure at 5e-7 torr.

1. Decay of ion signal to background at higher kinetic energy.
2. Second optimal KE at 10 to 20 eV.
3. Magnitude of second energy bump varies among experiments.

HOWEVER, three replicates of experiment 4 show difference in Ion-KE distribution pattern. The characteristic ion peak at 10-20 eV is small.



Significance and Applications

1. Abiotic synthesis of organic molecules in interstellar medium (ISM)

Plasma synthesis from HVIs between dust particles has been proposed to explain the observation of highly abundant organics in ISM.

2. Organic molecules on planetary bodies without substantial atmosphere

Understanding the synthesis of CN^- via HVIs helps to explain the sources of abiotic organic molecules on surfaces of airless planetary bodies, such as Ceres (De Sanctis et al, 2017).

3. Coevolution of planets and life in Hadean and Archean Earth

This experiment explores the effects of oxidation state on organic synthesis, providing insights for understanding the coevolution of planets and life.

Ongoing work:

1. Investigate the effects of targets (metal versus sample pellet) on ionization efficiency and Ion-KE distribution.
2. Investigate the optimal kinetic energy for molecular recombination and synthesis in plasma.
3. Add in atmosphere (N_2 or CO_2) to simulate an early Earth environment.

References

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