National Aeronautics and Space Administration

# Energetic Processing of Astrophysical Ice Analogs, Investigated via Two-Step Laser Ablation and Ionization Mass Spectrometry

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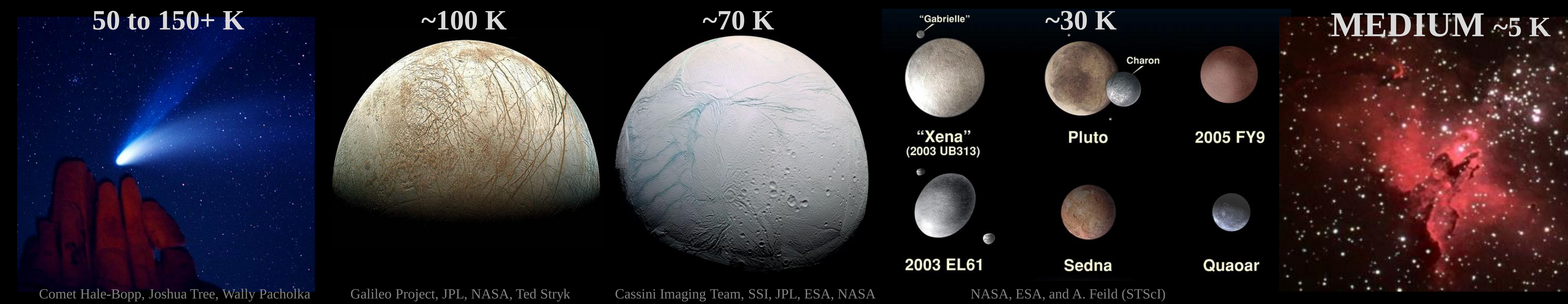
## Motivation: *Astrophysical Ices Exposed to Radiation*

***Can chemistry occur at 100 K? At 5 K?***

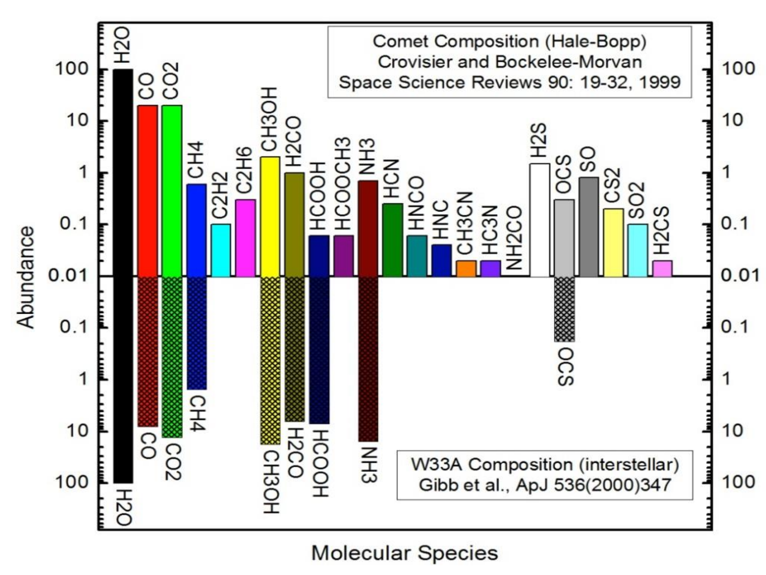
***Which reactive intermediates are important?***

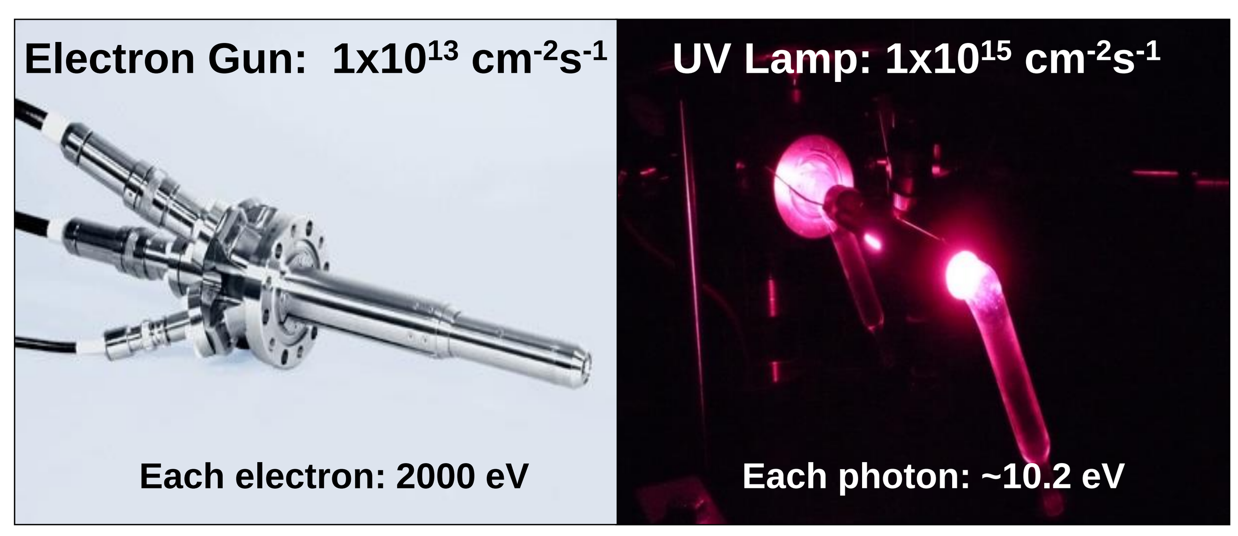
**Method:** **(1) Recreate these processes in the lab.**
**(2) Detect reaction products and intermediates with a novel mass spectrometry technique that allows for low-temperature analysis.**



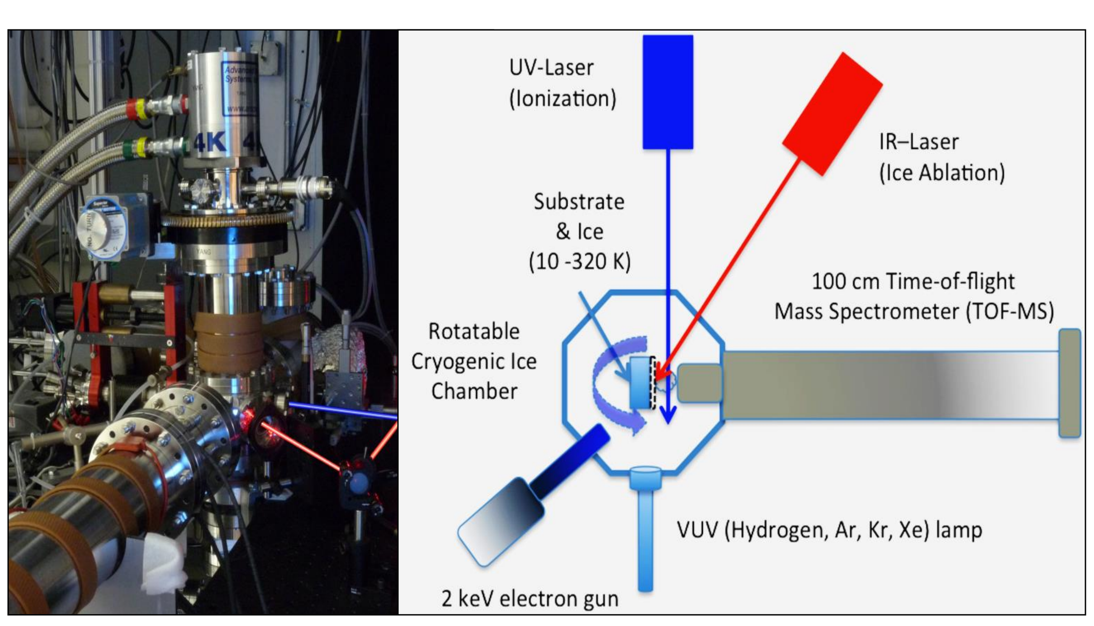

## 1. Prepare Ice Analogs and Expose to Space-Like Radiation

Comets and the interstellar medium (ISM) have similar compositions. During a typical lab experiment, we deposit and irradiate water ices containing relevant proportions of CO, $CO_2$, $CH_4$, $CH_3OH$, $H_2CO$, and/or $NH_3$ at temperatures <100 K.



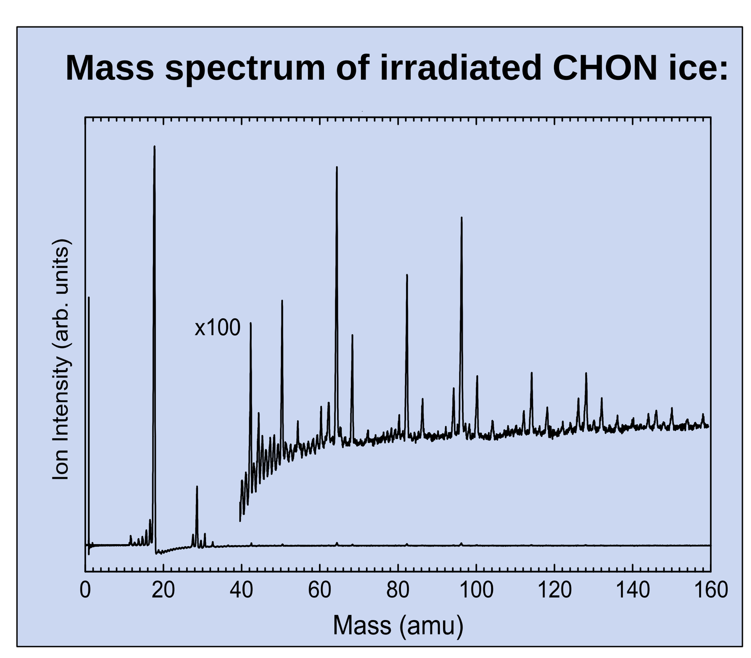

## 2. Detect Radiation Products Using Laser Ablation/Ionization Mass Spec.




Also see Gudipati, M.S. & Yang, R. 2012, *ApJ*, 756, L24.

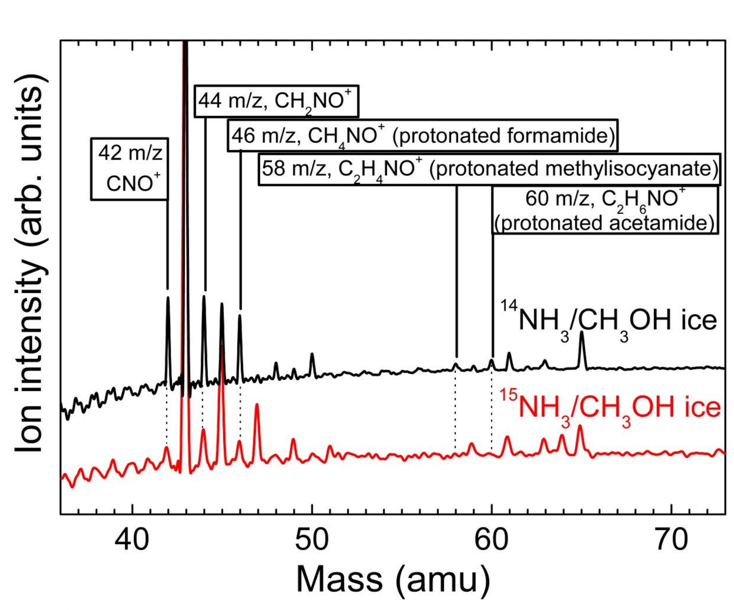
Our novel two-laser ablation and ionization mass spectrometry technique has several advantages:

- Enables *in situ* mass spectrometry at low temps (other mass spec methods rely on sample warming and processing).
- Complements and extends IR spectroscopy (where spectral congestion leads to uncertain assignments)




## 3. Assignment of Radiation Products

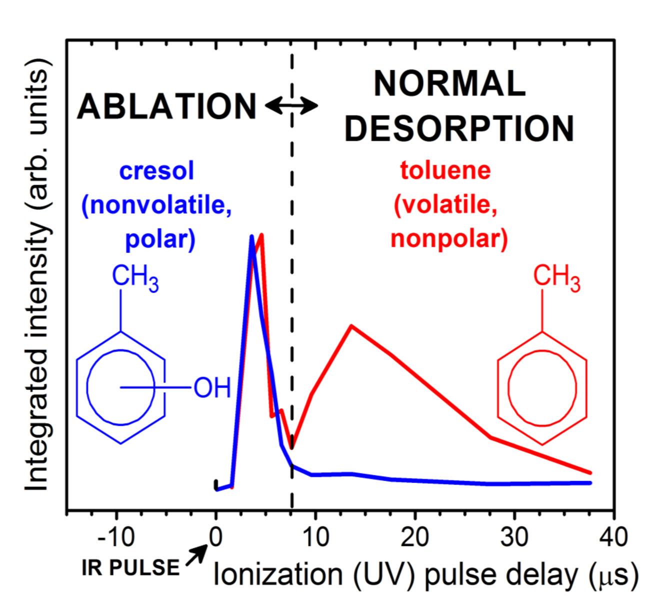
### Verification by Isotope Exchange




We have identified several new $CH_xNO^+$ species by comparing $^{14}NH_3$ (top trace) and $^{15}NH_3$ precursors in methanol ice samples (bottom trace).

Henderson, B.L. & Gudipati, M.S. 2014, *JPC A*, 118.29, pp. 5454-5463.
Henderson, B.L. & Gudipati, M.S. 2015, *ApJ* 800.1, 66.

### Verification by Volatility Analysis




Non-volatile species are found only in the initial ablative ejection (2-8 μs). Products found later in the plume's profile must be volatile (i.e. small or relatively nonpolar). **Our technique can provide structural information for ambiguous mass components!**

Henderson, B.L. & Gudipati, M.S. 2014, *JPC A*, 118.29, pp. 5454-5463.
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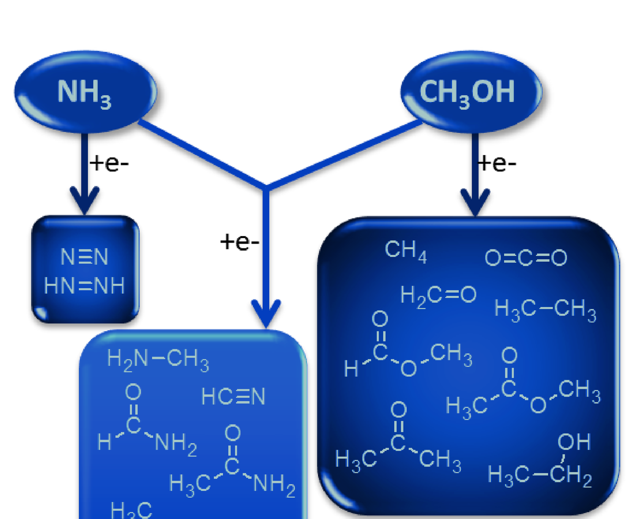
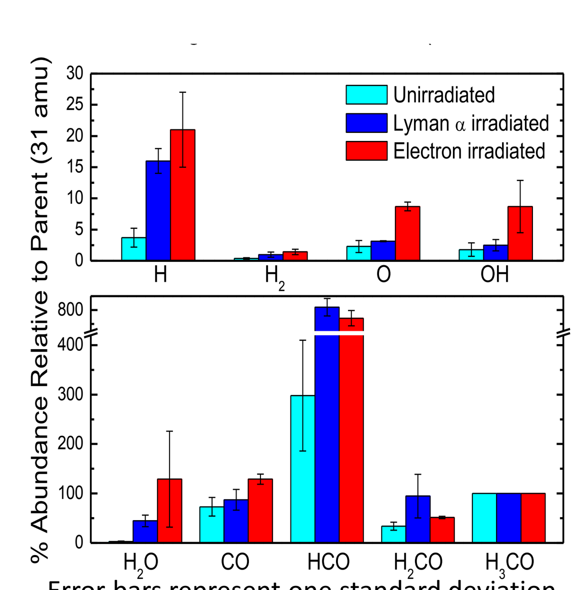
## 4. Summary of UV and e$^-$ Radiation Products of CHON Ices at 5 K



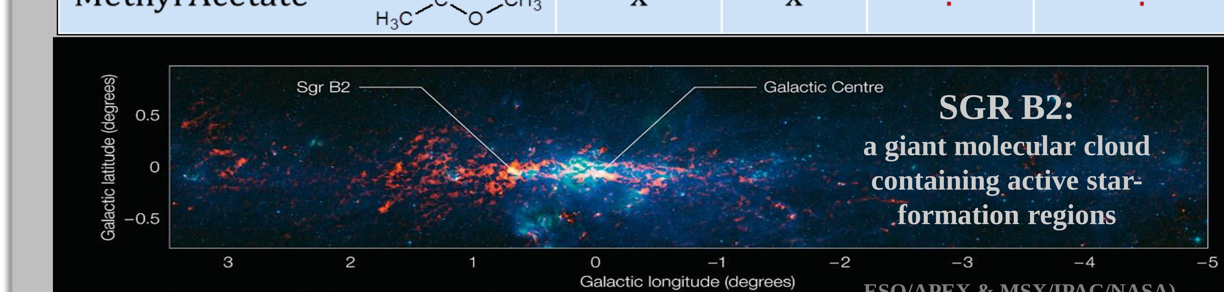

Error bars represent one standard deviation.

Simple ices containing ammonia and methanol produced many new complex organics upon irradiation (even at 5 K). Both UV and electron radiation sources led to the same reaction products in methanol ices, although e$^-$ radiation generally led to more $H_2O$ and CO and UV irradiation produced more HCO and $H_2CO$.

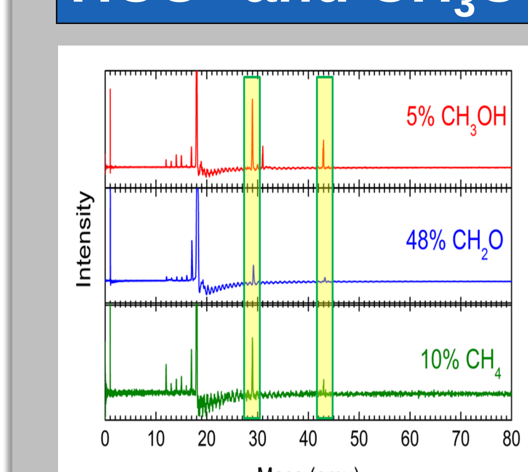
## Compare With Observational Data

Most of our detected species have been observed in space, but several have not yet been identified in comets. Our findings will help to guide future astronomical observations and investigations of viable low-temperature reaction pathways in astrophysical ices such as comets, KBOs, and other cold planetary and interstellar ices.

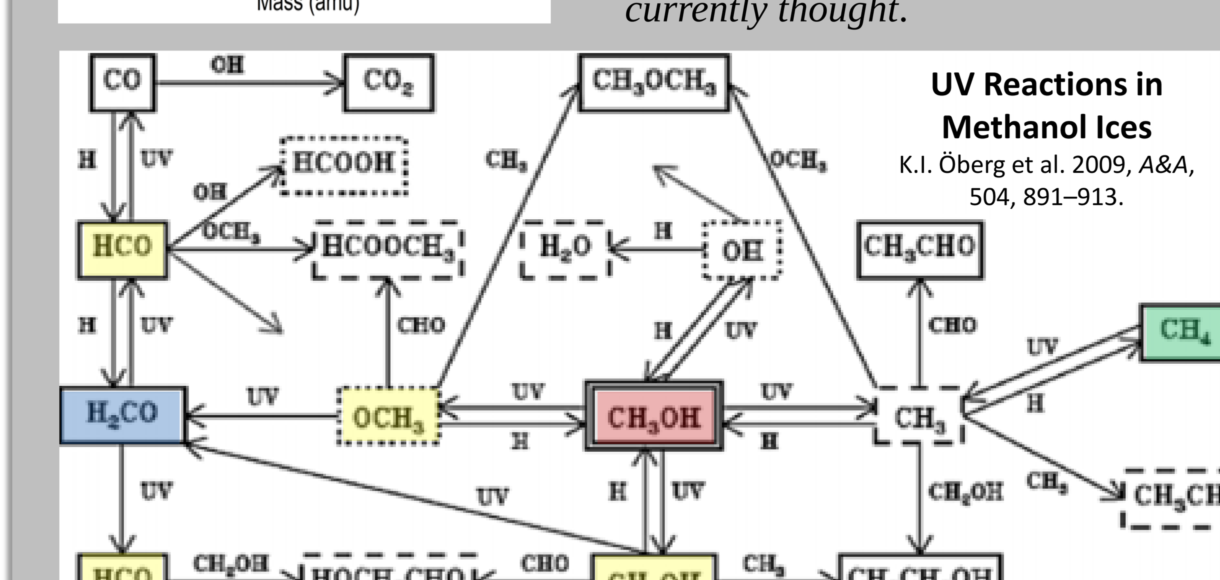
| Complex Organics | ISM | Sgr B2 | Comets | Meteorites |
|---|---|---|---|---|
| Formaldehyde $H_2C{=}O$ | x | x | x | x |
| Methylamine $H_2N{-}CH_3$ | x | x | x | x |
| Formamide | x | x | x | ? |
| Acetone | x | x | ? | ? |
| Acetamide | x | x | ? | ? |
| Methyl Formate | x | x | x | ? |
| Methyl Acetate | x | x | ? | ? |




## Compare With IR Spectroscopy Data: $HCO^+$ and $CH_3CO^+$ Are Key Intermediates




Every carbon-containing precursor we tested generated $HCO^+$ and $CH_3CO^+$ in water ices. $HCO^+$ and $CH_2OH^+$/$OCH_3^+$ (29 and 31 m/z) have long been identified as important intermediates in these ices (see diagram below), but *our low-temp experiments suggest that $CH_3CO^+$ (43 m/z) plays a more important role than currently thought.*

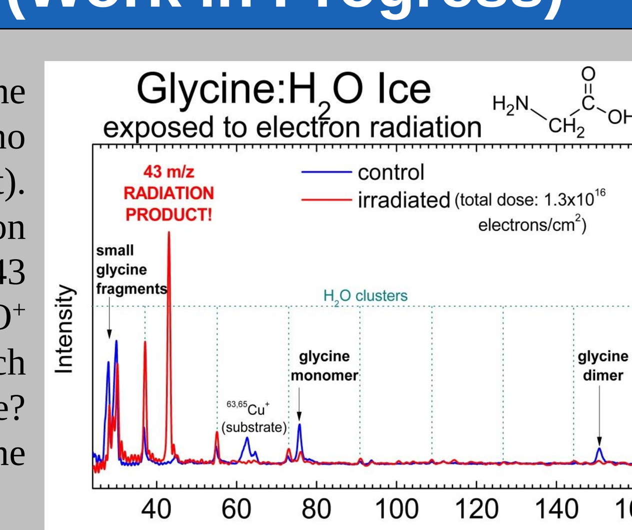



*Important low-temperature reaction pathways: how does the prevalent 43 m/z $CH_3CO^+$ intermediate fit into this scheme?)*

## Is $CH_3CO^+$ Also a Key Amino Acid Intermediate? (Work in Progress)

We have recently obtained the first mass spectrum of an amino acid encased in ice (right). Exposure to 2h of electron radiation led to a strong signal at 43 m/z. Is this signal due to $CH_3CO^+$ as seen above, or to $HCNO^+$, which is commonly observed in space? Isotopic verification of the assignment is currently underway.

This work will help to facilitate further observational searches for these species and will help to define the conditions required for production and survivability of complex organics in space.




*First ever mass spectrum of glycine encased in ice, 30 K. 43 m/z appears as a major radiation product – is it $CH_3CO^+$ or $HCNO^+$?*

Poster No. P-8

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