TWO-COLOR MALDI-TOF DETECTION OF COMPLEX ORGANICS IN ELECTRON-IRRADIATED ASTROPHYSICAL ICE ANALOGS. Bryana L. Henderson, NASA Postdoctoral Program Fellow, and Murthy S. Gudipati, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Blvd, Pasadena, CA 91109. (Bryana.L.Henderson@jpl.nasa.gov)

Introduction: Complex and biologically-significant organics have been detected in comets,[1] meteorites,[2] and in the interstellar medium,[3] and delivery of these molecules through impacts may have affected the emergence of life on Earth.[4] Here, we investigate the reactivity of typical cometary, outer solar system, and interstellar ice analogs under radiation environments.

Using a low-temperature two-stage IR laser desorption UV laser ionization technique developed in this lab,[5] we are able to eject irradiation products directly from the ice for analysis with time-of flight mass spectrometry. This low-temperature method circumvents traditional ice sample processing methods involving warming and acid extraction, and allows for detection of the very first reaction steps involved without compromising sample integrity, while supporting and enhancing prior infrared studies of irradiated ice analogs.

Methods: Three key components of interstellar and cometary ices – water, methanol, and ammonia – were deposited in various combinations onto a cryogenically-cooled copper substrate (5 – 150 K) under exposure to electron irradiation (2 keV, 5 μA). An infrared laser (2948 nm, 5 ns pulse) ablated the ice surface, ejecting the ice products toward an ultraviolet laser (355 nm, 5 ns pulse) which ionized the molecules for detection via time-of-flight mass spectrometry.

Results and Discussion: Pure ammonia and pure water samples underwent very few changes upon irradiation. Methanol-containing samples displayed rich chemistry, producing formaldehyde and ethanol at temperatures as low as 5 K (see **Figure 1** for a comparison of methanol and ammonia under the same irradiation conditions). Several fragment ions including CH_xO^+, $C_2H_xO^+$,$C_2H_xO_2^+$, and $C_3H_xO_2^+$ provided further evidence of methanol processing during electron bombardment. Analysis of electron-irradiated water/methanol ice mixtures revealed similar products. Molecular clusters composed of water, ammonia, and/or methanol molecules (up to n=~18) were common in all ices, and these signals aided mass spectral calibration.

Controlled temperature studies and plume desorption analysis further aided in species identification. For the temperature studies, a 90:5:5 H_2O:CH_3OH:NH_3 astrophysical ice analog was irradiated during deposition at 5 K for two hours and then warmed at a rate of 5 K min^{-1} to 150 K. These spectra (not shown) contained a series of peaks two mass units lighter than the methanol cluster series, which disappeared quickly at high temperatures relative to the methanol signals. These peaks were assigned to volatile formaldehyde-containing clusters. While warming to 150 K, all peaks decreased with temperature except those located at 61 and 45 m/z, which were assigned to the much less volatile methyl formate (protonated, 61 = $C_2H_5O_2^+$) and the methyl formate fragment (45 = HCO_2^+).

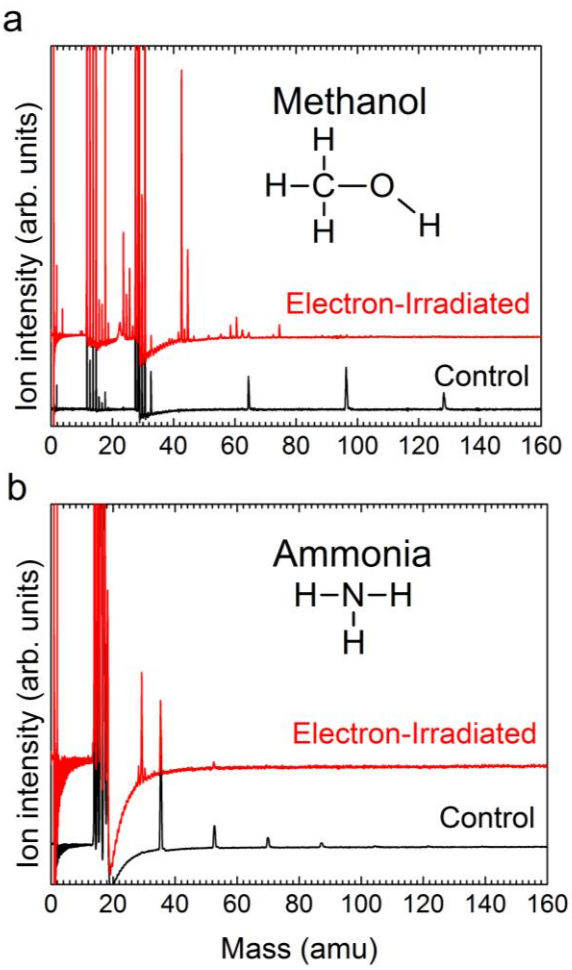

Figure 1. 2C-MALDI spectra of e-irradiated (red traces) and control (black traces) spectra for **a)** methanol and **b)** ammonia ices deposited at 70 K. Each ice was deposited for two hours at a chamber pressure of 5 x 10^{-7} mbar.

Signals found in 50:50 methanol:ammonia ices (CH_xN^+, CH_xNO^+, and $C_2H_xNO^+$) confirmed complex carbon-nitrogen species recombination. Protonated versions of methylamine (CH_3NH_2), formamide ($CH_3N{=}O$), and acetamide ($CH_3C(O)NH_2$) were detected. Nitrogen-containing irradiation products were confirmed through $^{15}NH_3$ isotope substitution studies (**Figure 2**).

Conclusion: For the first time, we report direct time-of-flight mass analysis of interstellar and cometary ice analog irradiation products at relevant temperatures *in situ*, without sample warm-up or adulteration. Complexity of irradiation products correlated with high concentrations of methanol. This increased availability of carbon-containing radicals likely results in increased recombination and formation of complex organics. Key compounds produced by electron irradiation of combinations of ammonia, methanol, and water ices include formamide, acetamide, and methylisocyanate, which may provide insight into the origin of biologically-complex organics.

References: [1] Bockelée-Morvan et al. (2000) *Astron. Astrophys., 353,* 1101. [2] Kvenvolden, K. et al. (1970) *Nature, 228*, 923; Engel, M.H. and Macko, S. (1997) *Nature, 389*, 265; Schmitt-Kopplin, P. et al. (2010) *PNAS, 107*, 2763. [3] Snow, T.P. and Bierbaum, V.M. (2008) *Ann. Rev. Anal. Chem., 1*, 229. [4] Chyba, C. et al. *Science, 249*, 366 (1990). [5] Gudipati, M.S. and Yang, R. (2012) *ApJL, 756*, L24.

Acknowledgments: This work was funded by a NASA Postdoctoral Program Fellowship (BLH), administered by Oak Ridge Associated Universities. Funding from NASA through NASA Astrobiology Institute and Planetary Atmospheres Grants to MSG enabled this work.This research was carried out at the Jet Propulsion Laboratory under a contract with NASA.

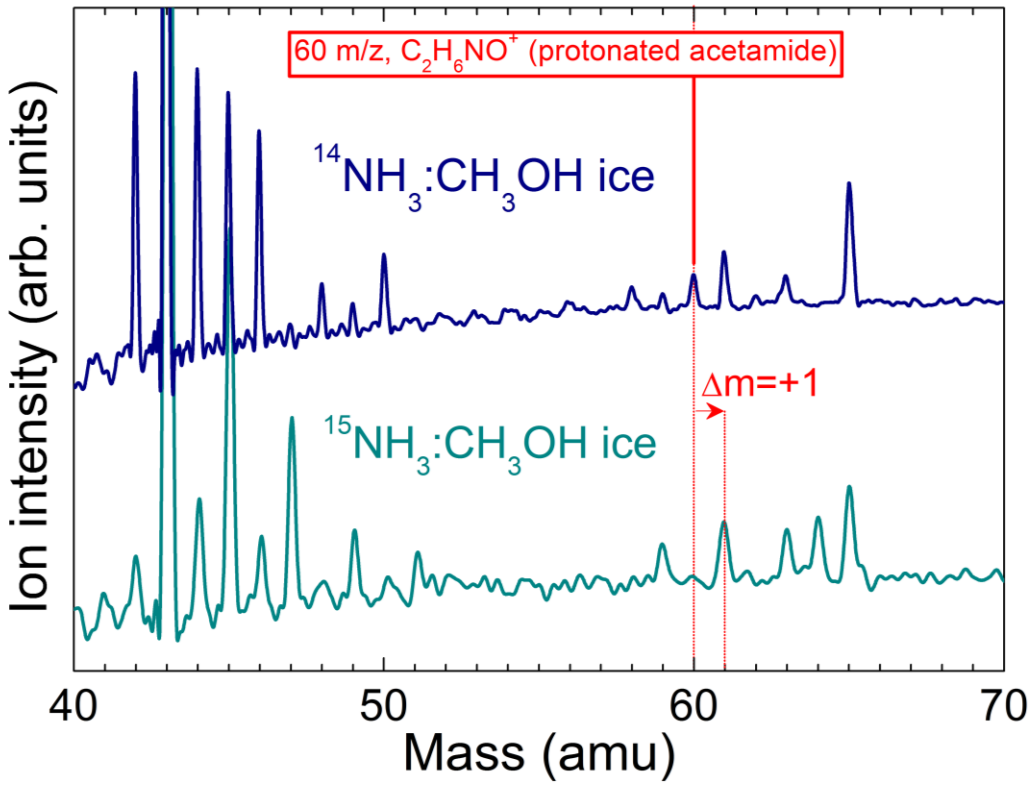

Figure 2. Isotopic comparison of electron-irradiated $^{14}NH_3/CH_3OH$ (top) and $^{15}NH_3/CH_3OH$ (bottom) ices. Acetamide (labeled) is shifted by 1 amu in the $^{15}NH_3/CH_3OH$ ices.