HYPERVELOCITY PLUME SAMPLING: EXPERIMENTAL EFFORTS AND ASTROBIOLOGY IMPLICATIONS.

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Introduction: The Saturnian moon Enceladus is thought to be one of the most ideal places to search for extraterrestrial, aqueous-based life. Enceladus has a global, subsurface ocean that is sandwiched between an outer, icy shell and the moon's rocky core. Fractures in the ice shell at the southern pole of Enceladus give rise to the plume, which expresses the subsurface ocean into space. The plume was interrogated by two mass spectrometry-based instruments aboard the *Cassini* spacecraft: the Ion and Neutral Mass Spectrometer (INMS) and the Cosmic Dust Analyzer (CDA). These instruments confirmed the presence of H_2, CH_4, and nanometer-sized silica grains, which are indicative of hydrothermal processes that occur at ≥90 °C. Both simple and complex organic molecules and ammonia were observed in the plume material.

Enceladus' plume enables ocean sampling with a flyby spacecraft (i.e. without the need to land and/or drill through kilometers of ice or wiggle through an ice crevasse). In several ways, flyby missions ease some of the constraints of orbital or lander missions; however, flyby measurements at hypervelocity (>1 km/s) present their own challenges. In order to obtain the most useful and detailed information from a future flyby mission, it is imperative to understand the processes that occur during hypervelocity sampling. This is particularly true for instruments employing impact ionization mass spectrometry, such as *Cassini's* CDA and the SUrface Dust Analyzer (SUDA) on *Europa Clipper*, that aim to survey the organic molecules at a particular target.

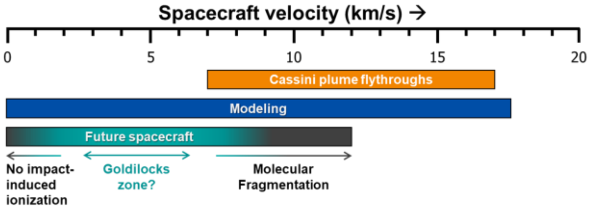

Figure 1. The velocities the Cassini spacecraft sampled the Enceladus plume might not be ideal for a future spacecraft. This research initiative aims to determine the velocity range needed to maximize molecular information.

It is not entirely clear at what impact velocities organic molecules will be volatilized, ionized, and/or fragmented, and it is important to determine if mass spectral patterns are sensitive to impact velocity in order to obtain high-fidelity information on the chemical species present in a sample. This is especially true if one of the mission's goals is to conduct molecular surveys for potential biosignatures. Figure 1 shows schematically the *Cassini* plume flythrough velocities; what velocities are achievable with first-principles modeling; and the velocity ranges of a future spacecraft that will enable volatilization and ionization (but not fragmentation) of organic molecules entrained within an ice grain.

Lab-based Analogue Experiments: Since the arrival of the *Cassini* spacecraft to the Saturn system in 2004, scientists have been trying to replicated the data produced by the spacecraft's instruments to improve the interpretation of results. For the CDA instrument, the method that has most accurately reproduced ice grain impact mass spectra is a laser-based analogue experiment in which laser-induced desorption/dispersion (LID) is coupled to a time-of-flight mass spectrometer (TOF-MS).[1] Using this combination of techniques, the CDA Science Team was able to identify and quantify salts and organic molecules (including high-mass organic molecules with heteroatoms) in the Enceladus plume ice grains.[2-6] Recent experiments have been used to predict optimal plume encounter velocities, which are 4-10 km/s for amino acids and 3-6 km/s for fatty acids.[7, 8]

Finding the Speed Limit of Biomolecules: The work detailed here is part of a research initiative that couples various experimental and theoretical techniques to better understand how impact velocity, impact ionization, and molecular fragmentation are connected. This research initiative includes theoretical modelling conducted at Caltech,[9, 10] and experimental work conducted with single ice grains at the University of California, San Diego [11, 12] and with an ensemble of molecules and water grains at the Jet Propulsion Laboratory. Experimental results from the JPL efforts will be presented.

Hypervelocity Ice Grain System (HIGS): The HIGS instrument at JPL is based on the lab-based instrument used by the CDA Science Team. Ions and neutrals are generated via IR laser-induced dispersion/desorption (LID) of a micron-sized liquid water jet located in a vacuum. The species produced range from bare, gas-phase molecules and atoms, through small hydrated clusters, to micron-sized water grains. The LID species then enter a TOF-MS, and charged species can be analyzed based on their mass-to-charge ratio. The initial HIGS instrument employed axial TOF-MS (aTOF) but is now being modified to use an orthogonal TOF (oTOF). The oTOF configuration allows for LID products (both charged and neutral) to impact a metal target plate before being mass analyzed. In this way, mass spectral distributions collected with the aTOF can be compared with the distributions measured with the oTOF. In other words, **the HIGS instrument can measure the mass spectral post-impact distributions of an ensemble of LID products travelling at 2-6 km/s**.

HIGS mass spectra and velocity distributions. The aTOF mass spectra of numerous solutions were collected while oTOF modifications were being designed and machined. Solutions of amino acids, fatty acids, mixtures of amino and fatty acids, and salt solutions were analyzed at various concentrations and at different TOF delays to characterize the velocity distribution of the LID products. These aTOF mass spectra will serve as a baseline for comparison to mass spectra collected post-hypervelocity impact.

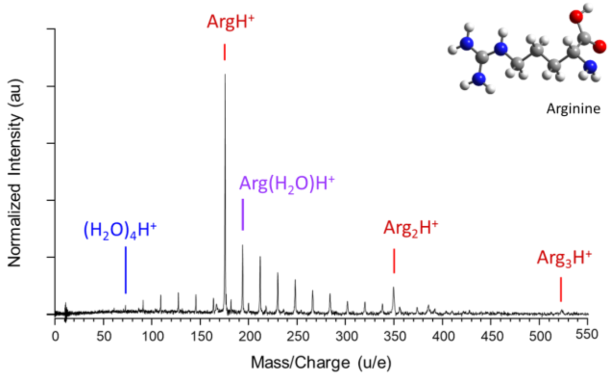

Figure 3. Axial time-of-flight cation mass spectrum of a 10 mM arginine (Arg) solution. The mass spectrum contains water, Arg, and water-Arg clusters. The distributions can be altered by changing source conditions.

Figure 2 presents a typical mass spectral distribution of a 10 mM arginine (Arg) solution, and demonstrates the three main product types of LID: water, arginine, and water-arginine clusters. While lower mass LID products are shown here, species ranging from bare atoms/molecules up to micron-sized grains are generated. LID product velocities can be calculated from experimental timings and the instrument geometry. By collecting mass spectra at different experimental timings, product velocities can be calculated.

Figure 3 presents the velocity distribution of a 10 mM arginine (Arg) solution, and indicates that protonated Arg ions are produced with velocities ranging from 2–5 km/s. By changing source conditions and settings, velocities of up to 6 km/s have been observed. The HIGS velocity distributions are within the range predicted by Klenner et al. [7, 8] to be optimal for amino acid impact ionization and also spans the velocity that theory predicts bare arginine to fragment (3-4 km/s). [10] Initial experiments with Arg solutions will lay the foundation on which to begin comparing analogue experimental and theoretical results to mass spectra collected after an impact at hypervelocity.

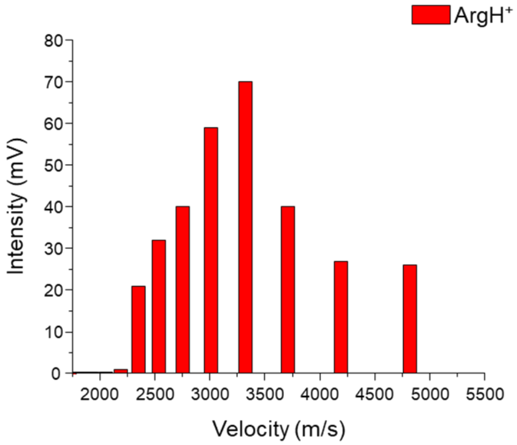

Figure 2: Laser-induced dispersion/desorption (LID) velocity distributions of a 10 mM arginine (Arg) solution. The velocities produced are within the range predicted to be optimal for amino acid impact ionization

Future post-impact experiments: Our initial experiments will focus on simple solutions of a single amino acid or fatty acid in deionized water. Once a few simple mass spectra are collected, complex solutions containing multiple amino acids and/or fatty acids in water and salt solutions (NaCl, $NaHCO_3$, and Na_2CO_3 for Enceladus-relevant solutions and NaCl, $MgSO_4$, and H_2SO_4 for Europa-relevant solutions) will also be analyzed to determine the effect of salts on organic survivability.

All of these mass spectra can be used to build an impact ionization library that can be used to further examine the data collected by CDA aboard the *Cassini* spacecraft and for the analysis of data obtained by SUDA aboard *Europa Clipper*.

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References: [1] Charvat, A. (2007) *PCCP*, 9, 3335. [2] Postberg, F. et al. (2009) *Nature*, 459, 1098. [3] Postberg, F. et al. (2011) *Nature*, 474, 620. [4] Postberg, F. et al. (2018) *Nature*, 558, 564. [5] Khawaja, N. et al. (2019) *MNRAS*, 489, 5231. [6] Klenner, F. et al. (2019) *Rapid Comm Mass Spec*, 33, 1751. [7] Klenner, F. et al. (2020) *Astrobio*, 20, 179. [8] Klenner, F. et al. (2020) *Astrobio*, 20, 1. [9] Jaramillo-Botero, A. et al. (2012) *Phys Rev Lett*, 109, 213201. [10] Jaramillo-Botero, A. et al. (2020) *Astrobio*, accepted, [11] Adamson, B. D. et al. (2017) *EPJ Tech and Instrum*, 4, 2. [12] Miller, M.E. et al. (2019) *EPSC Abstracts*, 13, EPSC-DPS2019-353-1.