USING IR SPECTROSCOPY TO OPTIMIZE ORGANIC DETECTION WITH A TWO-STEP LASER DESORPTION/IONIZATION TIME-OF-FLIGHT MASS SPECTROMETER. K. Uckert[1], N. J. Chanover[1], S. Getty[2], A. Grubisic[3], X. Li[4], W. B. Brinckerhoff[2], T. Cornish[5], D. Voelz[6], X. Xiao[6], D. Glenar[1] [1]New Mexico State University (Department of Astronomy, Las Cruces, New Mexico 88003; kuckert@astronomy.nmsu.edu), [2]NASA Goddard Space Flight Center (8800 Greenbelt Road, Mailstop 699, Greenbelt, MD 20771), [3]University of Maryland (Department of Astronomy, College Park, MD 20742), [4]University of Maryland, Baltimore County (1000 Hilltop Cir, Baltimore, MD 21250), [5]C & E Research, Inc. (9194 Red Branch Rd., Suite L, Columbia, MD 21045) [6]New Mexico State University (Klipsch School of Electrical and Computer Engineering, Las Cruces, New Mexico 88003)

Introduction: The detection of organics on other planetary surfaces provides insight into the chemical and geologic evolution of a Solar System body, and can indicate its potential habitability. Future payloads to high-interest astrobiology targets will necessarily be mass and power restricted, requiring compact, versatile, and multifunctional instruments. Infrared (IR) spectroscopy and mass spectrometry techniques are routinely included in landed or roving payloads for their ability to classify the elemental and mineralogical composition of a geologic scene *in situ*. In this study, we emphasize the astrobiologic potential of these instrument techniques, specifically the implementation of IR spectroscopy to optimize the detection of organic signatures with mass spectrometry. We analyze organically doped sulfate slurries with an IR spectrometer using on acousto-optic tunable filter (AOTF) as the dispersive element, and a two step laser desorption/ionization time-of-flight mass spectrometer (L2MS) with a tunable desorption IR laser whose wavelength range (2.7-3.1 μm) overlaps that of the AOTF IR spectrometer (1.6-3.6 μm). We explore the desorption IR laser wavelength dependence on the L2MS organic detection sensitivity in an effort to optimize the detection of high mass (>100 Da) organic peaks. A correlation between the maximum absorption of the NH functional group and broad hydration features - inferred from the IR spectrum - and the optimal IR laser configuration for organic detection using L2MS indicates that IR spectroscopy may be used to inform the optimal L2MS IR laser wavelength for organic detection.

Instrumentation: Our group has previously demonstrated the advantages of pairing an AOTF IR spectrometer and a laser desorption/ionization time-of-flight (LDTOF) mass spectrometer [1,2,3]. These efforts successfully demonstrated elemental and molecular detection capabilities of AOTF IR spectroscopy/LDTOF mass spectrometry; however, this configuration was not necessarily optimized for the detection of complex molecular structures associated with most biosignatures. The high energy required for a single laser pulse to both desorb and ionize a target typically fragments a large compound into its elemental constituents and leads to excessive ionization of mass species within the sample, particularly salts, which overwhelm the mass spectrum. A two-step LDTOF mass spectrometer preserves these biomarkers more frequently and allows for greater selectivity in the mass spectrum. Use of a tunable desorption IR laser allows for further optimization of high-mass species, especially when considering wavelength ranges associated with structurally bound hydration features and vibrational transitions of organic molecule functional groups, as can be characterized by the AOTF IR spectrometer.

IR Spectroscopy. AOTFs are low power devices that operate on the principle of diffraction in a birefringent crystal, and recent development by our group has demonstrated their versatility and portability [1,4,5]. We have developed a near-IR AOTF point spectrometer to measure the IR reflectance spectrum of geologic samples in the 1.6 - 3.6 μm range with a resolution of $\lambda / \Delta\lambda \approx 200 - 400$. A detailed description of the development and operation of this device is presented elsewhere [1,3,6].

The 1.6 - 3.6 μm range contains spectral signatures useful in identifying several common minerals relevant to terrestrial planetary surfaces, as well as the fundamental stretching and bending modes of ices and volatiles relevant to icy Solar System bodies including H_2O, CO_2, H_2S. Additionally, features corresponding to many of the basic organic compounds essential to life on Earth, such as characteristic group frequencies of amino, hydroxyl, and methyl groups, as well as O-H, N-H, and C-H stretching fundamentals lie within the 1.6 - 3.6 μm range [7].

Mass Spectrometry. Mass spectrometry is a powerful tool for identifying the elemental and molecular composition of geologic materials, and can be used to infer the mineralogy and characterize the organic carbon content within a geologic sample [8]. We investigate the organic detection capabilities of an L2MS, which separates the desorption and ionization functions into two distinct laser pulses to provide selectivity to key subclasses of organic species, such as aromatic hydrocarbons. We use a pulsed tunable OPO (Opotek Opolette 2731) IR laser (2.7 - 3.1 μm) for desorption, and an orthogonally positioned pulsed 266

nm Nd:YAG laser for ionization of the desorption neutral species. The use of distinct laser wavelengths allows efficient coupling to the vibrational and electronic spectra of the analyte in independent desorption and ionization steps, allowing for the mitigation of excess energy that can lead to fragmentation during the ionization process. A detailed description of the development, specifications, and sensitivity of this instrument is provided elsewhere [8,9,10].

Methods: We investigate the dependence the desorption laser wavelength has on the L2MS detection sensitivity of the aromatic amino acid tryptophan ($C_{11}H_{12}N_2O_2$). We prepared a slurry of epsomite ($MgSO_4 \cdot 7H_2O$) doped with 0.1 wt% tryptophan by dissolving tryptophan in water, adding powdered epsomite, and allowing the solution to recrystallize. The epsomite + 0.1 wt% tryptophan sample was measured with the AOTF IR spectrometer, as were pure tryptophan and epsomite powders, to identify hydration and organic functional group absorption features, as shown in Figure 1. Epsomite is expected to retain its structurally bound water over geologic time periods under Europa surface conditions [11], making it an ideal icy body analog for our laboratory studies focusing on the desorption of hydration features in vacuum.

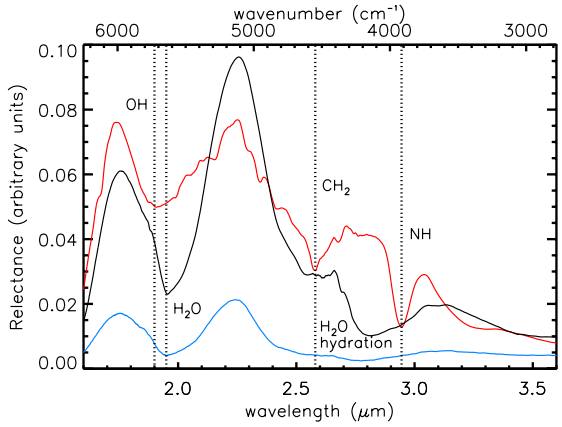

Figure 1: An IR spectrum of the epsomite 0.1 wt% tryptophan mixture, with annotations indicating the presence of absorbed and structurally bound H_2O and organic functional groups. The black trace corresponds the IR spectrum of the epsomite + 0.1% tryptophan mixture, the blue trace represents pure epsomite, and the red trace corresponds to pure tryptophan. Many of the weak, narrow absorption peaks from approximately 2.0 – 2.75 μm in the tryptophan spectrum are associated with aromatic CH vibrational features.

We collected mass spectra of the epsomite tryptophan mixture over the desorption IR laser wavelength range with a sampling frequency of $\Delta\lambda \approx 50$ nm near the broad hydration feature (2.75 – 2.9 μm), and $\Delta\lambda \approx 15$ nm near the narrow NH vibrational feature (2.9 – 3.0 μm). The laser energy was fixed to 0.85 mJ over the entire wavelength range. To compensate for shot-to-shot variability and temporal degradation of the signal, we first ablated the sample at a high laser energy (1.1 mJ) to remove loosely bound material. We collected approximately 50 shots for each laser configuration to minimize sample depletion through excessive ablation. The first 10 spectra at each IR laser wavelength value are removed from the average to compensate for signal instability caused by rapid ablation of surface material. An annotated mass spectrum of the epsomite mixture doped with 0.1 wt% tryptophan at an IR laser wavelength of $\lambda = 2925$ nm is presented in Figure 2.

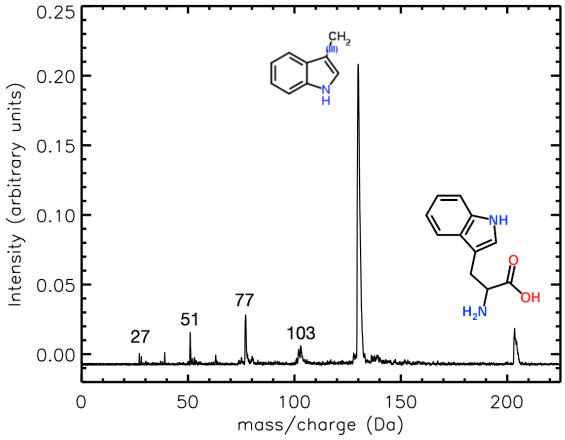

Figure 2: A mass spectrum of the epsomite sample doped with 0.1 wt% tryptophan collected by the L2MS with a desorption laser wavelength of 2.925 μm. The major tryptophan fragment is located at 130 Da, and the parent peak is located at 204 Da.

Results: The dependence of the maximum tryptophan signal strength on the IR laser wavelength is closely related to the vibrational absorption features presented in Figure 1. The sensitivity of the detection of the dominant tryptophan fragment (130 Da) to the IR desorption laser is presented in Figure 3. We quantify the 130 Da peak by integrating over the spectrum with boundaries defined by $\Delta m/z = 130$ Da ± 3 Da, which we empirically determined to contain all data points with intensities greater than 5% of the peak value for all IR wavelengths. The maximum tryptophan signal corresponds to an IR laser wavelength of 2.925 μm. This IR desorption wavelength is well correlated to the peak vibrational transition of the NH functional group at 2.94 μm. A broad secondary peak in the tryptophan signal variability with IR laser wavelength is centered at 2.825 μm, and is closely related to the broad H_2O hydration feature present in the epsomite IR spectrum shown in Figure 1.

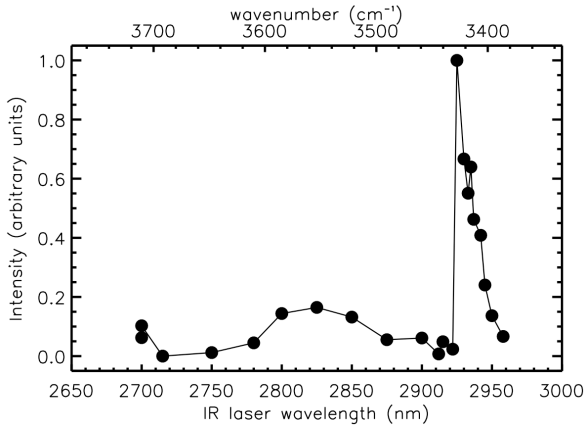

Figure 3: The dependence of the organic detection of the primary tryptophan fragment (130 Da) with IR desorption laser wavelength. The detection of tryptophan is optimized at a desorption laser wavelength of 2.925 µm, corresponding to the tryptophan NH vibrational absorption feature. A broader secondary peak from 2.75 – 2.85 µm corresponds to the broad H_2O hydration feature in epsomite.

Conclusions: We find a correlation between the optimal desorption laser wavelength for organic detection and the strength of the IR absorption features associated with the vibrational transitions of NH (2.925 µm), which is associated with the indole functional group – unique to tryptophan among amino acids, and broad hydration features (peak at 2.825 µm). Desorption of analyte is strongly dependent on the ability of the IR laser to couple with the molecular vibration and rotation modes, which are inferred from IR spectra. In Figure 4, we present the entire mass spectrum of the epsomite + 0.1 wt% mixture interpolated over all IR desorption wavelength values to demonstrate the dramatic increase in signal for all mass species when the desorption wavelength is tuned to certain IR spectral features. We also note the exclusive detection of some species (27 Da, 70 Da) at low IR wavelengths.

The IR desorption laser wavelength associated with the maximum signal is not exactly aligned with the peak absorption feature in the IR spectrum of pure tryptophan. Depletion of the sample following an initial strong detection of tryptophan at the tail of the NH vibrational feature (at 2925 nm) may have suppressed the signal for subsequent measurements. Uncertainties in the calibration of the tunable IR laser or AOTF may have introduced systematic errors. We also consider the possibility that the peak IR vibrational absorption feature has shifted following crystallization with epsomite. To better characterize this phenomenon, we plan to measure a suite of organically doped samples with the AOTF IR spectrometer and L2MS.

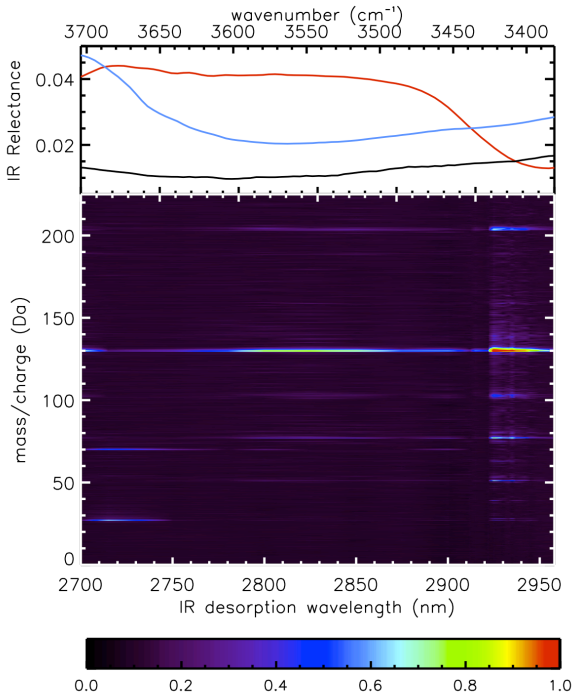

Figure 4: The dependence of the mass spectrum on the IR desorption wavelength. The signal is observed to increase when the IR desorption laser wavelength is tuned to IR spectral features.

IR spectroscopy and mass spectrometry are well suited to identify the elemental and organic constituents of a sample and characterize its mineralogy *in situ*. We present the unique organic detection capabilities of L2MS, and demonstrate the value of using these techniques in a complimentary manner to optimize the detection of organics on other planetary bodies.

References: [1] Chanover N. J. et al. (2013) *Aerosp. Conf. Proc.,* 1—14. [2] Getty S. A. et al. (2012) *International Workshop on Instrumentation for Planetary Missions*, Abstract # 1638. [3] Chanover N. J. et al. (2012) *International Workshop on Instrumentation for Planetary Missions*, Abstract #1683. [4] Uckert K., et al. (2014) *Aerosp. Conf. Proc.*, 1—12. [5] Chanover N. J. et al (2014) *International Workshop on Instrumentation for Planetary Missions.* [6] Tawalbeh R. et al. (2013) *Opt. Eng.*, 52, 1–10. [7] Pieters C. M. and Englert P. A. J. (1993) *Remote Geochemical Analysis: Elemental and Geological Composition*, Cambridge University Press. [8] Getty S. A. et al. (2014) *Aerosp. Conf. Proc.*, 1 – 6. [9] Getty S. A. et al. (2014) *International Workshop on Instrumentation for Planetary Missions*. [10] Getty S. A. et al. (2013) *LPS XLIV*, Abstract #1719. [11] McCord T. B. et al. (2012) *JGR*, 106, 3311–3319.