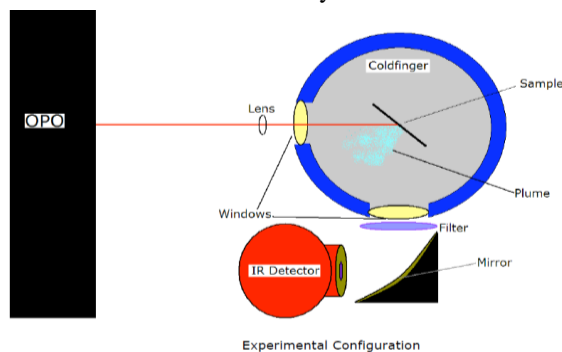**LASER DESORPTION INFRARED SPECTROMETRY FOR ICY MOON SURFACES.** N. M. Figewski[1], L. W. Beegle[2], and L. S. Sollitt[1,3], [1]The Citadel, The Military College of South Carolina, Charleston, SC 29409; [2]NASA/Jet Propulsion Laboratory, Pasadena, CA 91109; [3]The Planetary Science Institute, Tucson, AZ;.

Introduction: The majority of the satellites of the outer solar system are dominated by icy surfaces. The identification of the bulk composition (~1%) of these ices has been done through remote observations including Near Infrared, Infrared (IR) and gamma-ray spectroscopies. A more thorough understanding the chemistry of these surfaces, specifically for astrobiological research, is best done via in situ missions which can analyze surface material to much higher sensitivities which result in a better scientific understanding of the physical conditions and history of the surface. However, *in situ* analysis is an expensive undertaking especially when complicated mobility or sample acquisition and handling hardware is required. We present a method for fast, accurate identification of chemical species at standoff distances to greater sensitivity than possible with traditional standoff techniques. Our technique combines wavelength dependent laser desorption with IR emission spectroscopy for unique identification of material on the surface of icy bodies.

**Figure 1** Experimental set up.

Laser Desorption-Infrared Spectroscopy (LDIR) takes advantage of the characteristic vibrational frequencies of water in the mid-infrared. A laser pulse at one of these frequencies is resonantly absorbed by the ice, resulting in the explosive desorption of a warm (>300 K) plume of material from a cold surface (~100 K) [1,2]. This plume can consist of the bulk matrix material, minor chemical species, or a combination of both depending on the incident wavelength and power (we refer to this as selective vs. non-selective desorption) [3]. The contrast between the radiated spectrum and the cold surface provides enough signal such that the detection may be done from substantial standoff distances. Chemical species present in the ice will radiate at characteristic IR frequencies that can be detected by an IR detector. LD-IR requires significantly less power than LIBS or Matrix assisted laser desorption mass spectroscopy (MALDI) and is much more sensitive than passive IR reflectance spectroscopy. The threshold laser pulse energy density for LDIR can be as low as 120 mJ/cm^2 as opposed to 5 J/cm^2 for other techniques. This low energy process allows for the detection of larger molecules that would be broken apart in LIBS or MALDI.
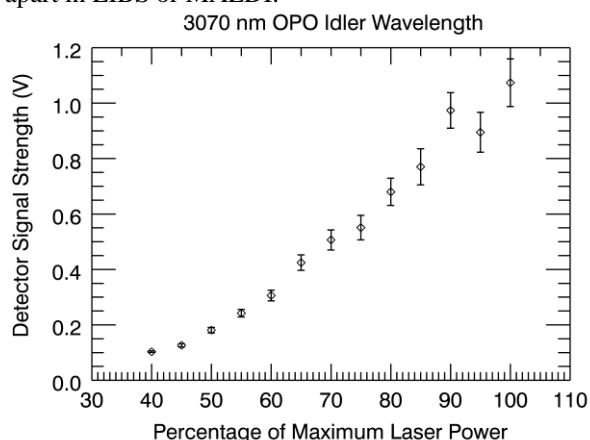
Figure 2 energy needed to desorbs material from water ice when incident wavelength is 3070nm.

Method: Ice was frozen on a sample holder, and attached to a cold finger. The sample was dipped into liquid nitrogen before being placed into the vacuum chamber (Figure 1). The OPO was focused with one CaF$_2$ lens (>90% transmission from 3000-3500nm). This passed through a GeSe (>95% transmission) window into the chamber, then struck the ice sample. The photons generated from the desorption plume passed through another GeSe window, then traveled through a longpass band filter (4.73 – 9.30 μm, >95% transmission) in order to assure no false signals from the laser were seen. The photons were focused by a protected gold-plated off-axis parabolic mirror into a Teledyne Judson J15D12 HgCdTe photoconductive detector. Voltage pulses from the detector were read through a National Instruments DAQPad 6016 into a custom LabView data collection system. Data were collected at 200 kHz.
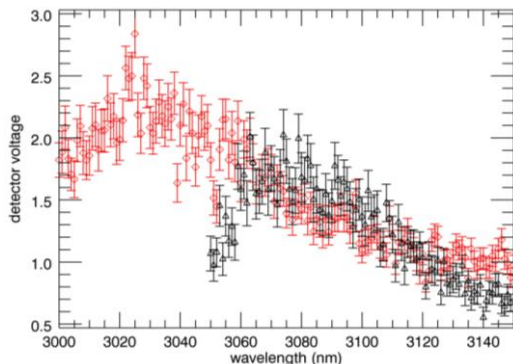
Figure 3: Detector voltage as a function of incident laser wavelength for D_2O (red) and H_2O (black). The "D_2O" peak is due to desorption of amorphous ice that has condensed onto the D_2O substrate.

Experimental results: In our first set of experiments, we varied laser fluence, while keeping the laser at 3070 nm incident on cryogenic (<100 K) water ice. In the second series we scanned through a series of wavelengths at constant energy to map the desorbed plume intensities through an absorption feature.

For the first series of experiments, we chose an OPO idler wavelength of 3070 nm and increased the power of the pulse in steps from 61.38 mJ/cm^2 to 153.46 mJ/cm^2. We observed a significant increase in the detector signal as power increases (Figure 2). Detector voltage is directly related to desorption yield, as more photons will be generated if there is a larger amount of material being desorbed into the plume. We begin to see a significant (above detector noise) desorption signal at approximately 50% laser power, or about 75 mJ/cm^2.

In the second series of experiments we varied the laser wavelength in 1 nm increments between 3050 nm and 3150 nm at 96.5% laser power. Actual fluence values varied with wavelength. For each wavelength, 98 shots were fired at 20 Hz. The corresponding data point is the ensemble average of all of the recorded detector voltages. Our detector was not synched with the laser pulse emission, with the result that we were effectively "sampling" our plume at a random time in each desorption event. In the runs with H_2O (the black points in Figure 2), we observed a maximum in the desorption yield at about 3070 nm, which is what one would expect for the O-H stretch feature in cryogenic crystalline ice. As a blind test of the method, we did a series of runs with D_2O (which has no absorption feature in this wavelength range) between 3000 nm and 3150 nm, in 1 nm steps. We observed (red points in Figure 2) a pronounced desorption feature centered at approximately the O-H stretch absorption feature for amorphous ice [4].

It may be that in the relatively weak (~10 mTorr) vacuum of our chamber that H_2O vapor was re-deposited onto the D_2O substrate. At the temperatures and pressures present in the chamber, the deposited material would have formed into amorphous ice. After being struck with the laser light, the water must have re-deposited very quickly back onto the desorption site.

At the end of the scan damage was observed on the H_2O ice sample (figure to the right, inside the oval), and presented as a narrow oval feature near the top of the puck. The oval shape is due to the incidence angle of the laser on the ice. No similar feature was observed on the D_2O sample.

Conclusions: The work here represents the beginnings of an effort to apply the techniques of laser resonant desorption to the detection of interesting biogenic compounds in planetary ices. We demonstrated desorption of water ice in two distinctly different manners: first, by detection of IR emission of the desorbed plume with a photoconductive detector; second, by generating laser damage on an H_2O sample but not a D_2O sample (non-resonant absorption would have generated damage in both samples).

The conditions of this experiment were far from ideal: 45° incidence angle, rough ice surface, and poor vacuum. That we still measure a desorption threshold at approximately 75 mJ/cm^2 indicates that LDIR may well be an effective technique to search for astrobiologically interesting compounds on icy worlds.

Future experiments will add a mid-IR spectrometer to measure emission spectra of desorbed plumes, and will extend from pure water ice to binary mixtures in order to directly test the viability of observing compounds in ice.

References: [1] Chou, M., J. Arenberg and L. Sollitt, AIAA Space 2004 Conference (2004). [2] Focsa, C., B. Chazallon and J. L. Destombes, Surface Science 528(1-3): 189-195 (2003). [3] Focsa, C., et al, J. Phys-CM 18(30): S1357-S1387 (2006). [4] Figlewski N. M. and Beegle L. (2011) *Laser Desorption Infrared Spectroscopy for Icy Moon Surfaces*.