LASER DESORPTION INFRARED SPECTROSCOPY: A PROOF OF CONCEPT STUDY FOR FUTURE ICY WORLD EXPLORATION S. K. Long[1], L. W. Beegle[2], and L. S. Sollitt[1,3], [1]The Citadel, 171 Moultrie St., Charleston, SC, 29409 slong1@citadel.edu, [2]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109 luther.w.beegle@jpl.nasa.gov, [3]Planetary Science Institute, 1700 E. Fort Lowell, Suite 106, Tucson, AZ 85719 Luke.Sollitt@citadel.edu

Introduction: Identifying biologically significant compounds is a prime objective for any spacecraft sent to explore icy worlds. Detection of these materials in ice is one of the most important goals for a mission to bodies such as Europa. Using Laser Desorption Infrared Spectroscopy (LDIR), we intend to provide a cost effective method for accomplishing this task on future missions. Through implementation of a tunable pulsed Optical Parametric Oscillator (OPO) Laser operating in the 3-3.4µm range, we were able to demonstrate identification of desorption in frozen samples of water and other compounds. Water exhibits very strong absorption in this range [1]. This, in combination with a significant reduction in laser pulse length, would result in much lower energy requirements for such an instrument. Future investigations include samples consisting of binary mixtures of known organic dopants and water.

Methods: The set-up used in this series of experiments is shown in Figure 1. An OPOTEK mid-IR Optical Parametric Oscillator (OPO) supplies tunable laser light between 3000 and 3450 nm. The light passes through a pellicle beam splitter (attenuating it by 70%), and is then focused down by a [material] lens to a point inside the Oxford Instruments Optistat DNV cryostat. Typical operating pressure in the cryostat was on the order of 3-5 mTorr; the sample was kept at LN2 temperature: approximately 77K. The cryostat windows are ZnSe in order to be transparent to mid-IR and LWIR light. Light from the desorption plume passes out of the cryostat exit window, is gathered by a parabolic mirror, and then directed through a longpass (4.73 – 9.30 µm) filter into a Teledyne Judson J15D12 MCT single-point photoconductive detector.

Data collection was done with a high-rate (2 GHz) digital oscilloscope. The oscilloscope can only record data at 8 bits of resolution; however, we correct for this and for variable output of the OPO by taking 100 desorption shots per data point. The large number of shots per data point ensured that a high-confidence average laser fluence and desorption signal could be attained, even given the limitations of the equipment.

Sample: A cup 1.5 cm in diameter is chilled outside the cryostat chamber to 77 K through immersion in LN2, then filled with pure water. Typically, the water freezes so quickly that a characteristic point will form in the center of the sample; this is smoothed out by a copper rod into a relatively flat ice sample. The sample cup, already attached to the empty cryostat N2 reservoir, is then inserted into the cryostat housing with the sample aligned vertically, and so that the laser light has an incidence angle on the surface of approximately 45°. For the work done here, pure water samples were used, but given the relatively low vacuum provided by the roughing pump, our samples were subject to organic contamination.

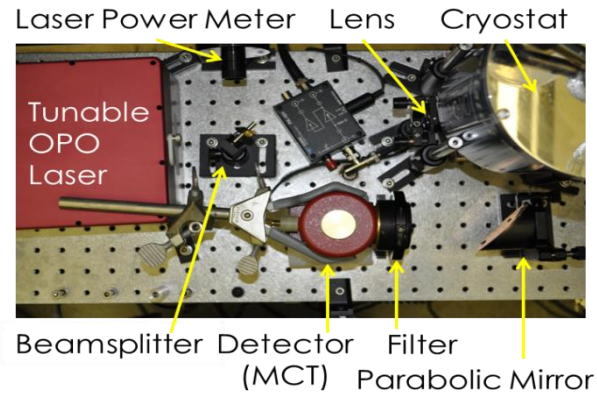

Figure 1. Experimental setup

Results: A significant peak in detector response can be observed at the wavelength coinciding with the O-H stretch wavelength for frozen water [2]. Figure 2 shows detector response (in integrated volts-seconds) during a wavelength scan though the entire range of the OPO. The expected characteristic peak for the desorption of water appears; there is also a small secondary peak from desorption in the C-H stretch region: the contaminants in (or on top of) our water ice.

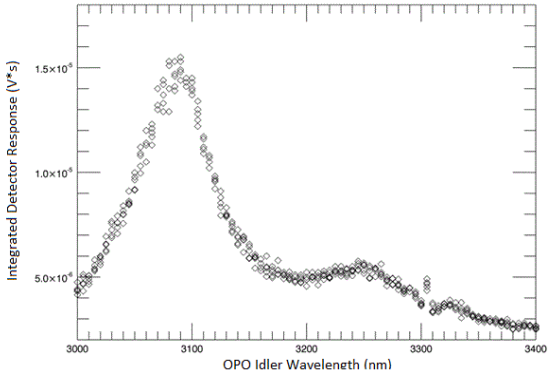

Figure 2. Detector signal from pure water desorption**.**

We explored the desorption threshold for water by scanning over the wavelength range of 3060 nm to 3120 nm at different laser powers, beginning at 70% laser power and continuing until the signal disappeared. Figures 3 and 4 show the results of these scans. Each data point corresponds to 100 individual desorption plumes. The uncertainties in these figures are statistical. Figure 3 shows the higher-intensity desorption profiles with wavelength over the range of 3060 to 3120 nm. The peaks are reasonably obvious down to 40% laser power. The maximum laser power is approximately 1.7 mJ/pulse, corresponding to about 150 mJ/cm^2 given our spot size. Figure 4 is a blow-up of the lower-intensity profiles, showing that the desorption peak is still reasonably clear down to 30% power. The curve for 25% might seem just about flat, but a blow-up of that curve still features a desorption peak. Below this laser intensity we seem to be dropping below the detection threshold of our photoconductive detector. A laser intensity of 25%, then, corresponds to an upper limit for a desorption threshold for water ice at approximately 77K.

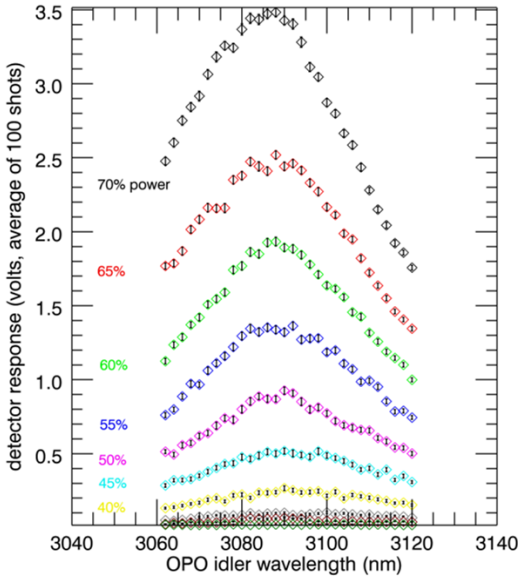

Figure 3. Desorption peaks at high laser intensity.

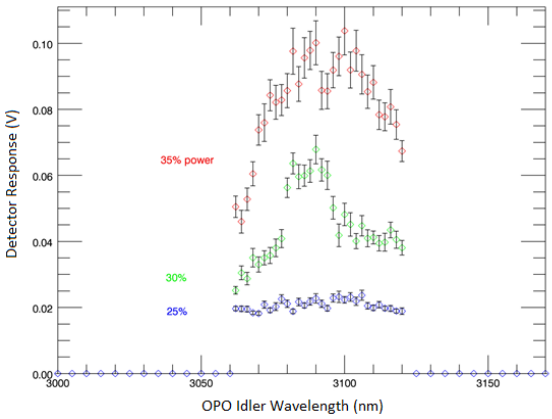

Figure 4. Desorption peaks at low laser intensity.

Conclusions: High detector response at water's O-H stretch wavelength indicates the presence of laser desorption at the sample's surface. Contrary to expectations, desorption is seen throughout the wavelength region of the desorption peak at all laser intensities where desorption is seen. The search for a desorption threshold yielded an upper limit of no more than approximately 25 mJ/cm^2. This is a significant reduction in required power compared to previous work in probing frozen samples [3]. This smaller power requirement could mean a sizeable reduction in cost and complexity of such a system on future missions.

References: [1] Focsa C., Chazallon B., Destombes J. L. (2003) *Surface Science, 528*, 189-195. [2] Schriver-Mazzuoli L., Schriver A., Hallou A. (2000) *Journal of Molecular Structure, 554*, 289-300. [3] Toftmann B., et. al. (2005) *Applied Surface Science, 247*, 211-216.