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ABSTRACT

To probe the molecular composition of a remote target, a laser is directed at a spot on the target, where melting and evaporation occur. The heated spot serves as a high-temperature blackbody source, and the ejected substance creates a plume of surface materials in front of the spot. Bulk molecular composition of the surface material is investigated by using a spectrometer to view the heated spot through the ejected plume. The proposed method is distinct from current stand-off approaches to composition analysis, such as Laser-Induced Breakdown Spectroscopy (LIBS), which atomizes and ionizes target material and observes emission spectra to determine bulk atomic composition. Initial simulations of absorption profiles based on theoretical models show great promise for the proposed method. This paper compares simulated spectral profiles with results of preliminary laboratory experiments. A sample is placed in an evacuated space, which is situated within the beam line of a Fourier Transform Infrared (FTIR) spectrometer. A laser beam is directed at the sample through an optical window in the front of the vacuum space. As the sample is heated, and evaporation begins, the FTIR beam passes through the molecular plume, via IR windows in the sidewalls of the evacuated space. Sample targets, such as basalt, are tested and compared to the theoretically predicted spectra.

Keywords: directed energy, asteroid, infrared, FTIR, laser, standoff, composition, spectroscopy

1. INTRODUCTION

1.1 Spectroscopy

Spectroscopy refers to a process where a light passing through a sample is analyzed to determine composition. The basis of this process rests on the fact that each molecule has specific, characteristic wavelengths of light that they absorb from an external source. One way to model the fundamentals of spectroscopy is to recognize that the binding force between atoms in a given molecule is restorative, proportional to the displacement of the atoms, and thus obeys Hooke's Law:

\[ F = -kx \]  

Where \( F \) is the force of the bond, \( k \) is a constant intrinsic to the system, and \( x \) represents the displacement from equilibrium position. Each molecular bond has a different \( k \) value, and, thus, a different restorative force for a given displacement. An electromagnetic wave applies a time varying electric field to the molecules, and displaces the component atoms based on uneven distributions of electrical charge within the molecule. The response of the molecular bond’s restoring force creates a harmonic oscillation with either a single frequency and its corresponding amplitude, or a summation of multiple frequencies with corresponding amplitudes. The potential energy contained within these bonds in this model is given by:
\[ U = \frac{1}{2} kx^2 \]  \hspace{1cm} (2)

From this equation, it is clear that a higher amplitude (or higher maximum displacement) corresponds to a higher energy contained by the bond. This energy, exchanged between kinetic and potential during oscillations, is originally provided by the time varying incident electromagnetic field. The amplitude of oscillation, which is directly proportional to the energy absorbed from an electromagnetic wave, is maximum when the frequency of the light driving the oscillation is equal to the resonant frequency of the system. The resonant angular frequency is given by:

\[ \omega = \sqrt{\frac{k}{m}} \]  \hspace{1cm} (3)

Where \( m \) = reduced mass of the atoms in the bond. Every bond with a given \( k \) value (relating to bond strength), has a corresponding \( \omega \) (angular frequency) of electromagnetic radiation that will maximally drive the molecules. The molecules will then completely absorb light at this frequency. If one passes a broad distribution of light frequencies through a sample, there will be specific troughs in the electromagnetic frequency spectrum that correspond to characteristic wavelengths of various chemical bonds within the sample, allowing one to determine the sample’s molecular composition.

### 1.2 Standoff Spectroscopy and R-LEMA

While spectroscopy is a highly developed and useful form of composition analysis, one challenge is to employ this technology outside of an FTIR machine and analyze samples at a greater distance. This process of performing spectroscopy on objects distant from the measurement device is called “standoff spectroscopy.” One recent technological breakthrough in standoff spectroscopy is called Laser-Induced Breakdown Spectroscopy (LIBS). LIBS uses a pulsed laser to periodically heat up a small point on the surface of a sample. When the sample is heated, many electrons of the sample are ionized, creating a plasma, and many of the remaining electrons are excited. During the short period between laser pulses, the excited electrons drop back down to lower energy levels, emitting characteristic wavelengths of light in the process.\(^1\) This method has proved fairly successful in applications of standoff spectroscopy, and has thrust itself into the public consciousness through applications such as the Mars Rover.

R-LEMA is an alternative standoff composition method. This process also uses laser power to agitate the target for spectroscopy, yet differs from LIBS in that the laser is consistently applied at lower intensity, around 10 MW per square meter.\(^2\) At this flux, the target quickly heats to about 2500 K and sublimation of the surface occurs. As the ablation continues, a plume develops, a bore is dug into the surface of the asteroid, and the spot begins to emit blackbody radiation.\(^2\) The radiating background is then used as a light source for spectroscopy, which can be performed via fiber optic photonics sensing.

There are several advantages that this method provides. First, the lower intensity laser leaves entire molecules intact, whereas the ionization of emitted particles conceals some information regarding the molecular composition of the asteroid.\(^2\) Additionally, the R-LEMA method allows for sub-surface composition analysis due to the removal of superficial substance during ablation. Finally, R-LEMA provides for a greater standoff distance than contemporary spectroscopy methods, such as LIBS.\(^2\)

### 2. LABORATORY SETUP

The sample in question rests inside a vacuum chamber, which provides an environment of about 5 mTorr to simulate outer-space conditions. This chamber, which contains ZnSe window ports to permit the passage of an infrared beam, is placed inside a Magna-IR 750 FTIR Spectrometer.

To verify the R-LEMA method and apply it in a laboratory setting, a vacuum test chamber shown in Figure 1 was designed to simulate the conditions of outer space. When a high-power laser ablates a sample under
vacuum, a cloud of ablated particulates forms within the chamber. Given that the density of particulates is sufficiently high, spectra can then be performed by a standard transmission FTIR spectrometer whose beamline passes through the plume in the evacuated space. Key features of the chamber include its ability to be evacuated (Figure 2) and facilitate two beams: one laser for ablation, which passes through a quartz window (Figure 3) and another for spectroscopy, which passes through a ZnSe window (Figure 4). The light source for standoff infrared spectroscopy, in the future, will be the black body radiation of the ablated rock, however, in these preliminary experiments, we use a separate laser source from the spectrometer.

![Figure 1. R-LEMA spectroscopy test chamber design](image1)

The chamber was designed to be evacuated to the mTorr range and operate with standard vacuum equipment shown in Figure 2.

![Figure 2. Standard KF40 flange for vacuum connection](image2)

To ablate the sample, up to 200 W of continuous-wave (CW) 808 nm laser power was focused onto a sample within the chamber, creating an ejection plume. The path of this high-power beam is depicted by the red arrow in Figure 3.

In order to carry out this process, an FTIR (Fourier-Transform InfraRed) spectroscopy machine is used (Magna-IR 750 FTIR Spectrometer). The most pertinent components of an FTIR machine consist of a hood in which the sample is placed, a light source emitting a broad spectrum of light (chiefly in the infrared), and a detector. The source produces light which is focused into a beam, then passed through the sample to be recollected by
Figure 3. Lens assembly and XYZ stage for 200-W ablation laser

Figure 4. Port designed with a ZnSe window for the spectroscopy measurement beam

a detector. The path of this light beam is depicted by the green arrow in Figure 4. The spectrometer sends an infrared beam through a KBr beamsplitter, goes through the sample, and eventually is collected by a PbSe photoconductive detector. OMNIC FTIR software then performs Fourier analysis on the data and produces a plot of absorbance (AU) vs. wavenumber (cm$^{-1}$), which can be compared to the spectra of absorbed wavelengths for known substances in order to determine the composition of the sample using a library of known absorbance profiles.

Figure 3. Lens assembly and XYZ stage for 200-W ablation laser

3. PRELIMINARY EXPERIMENTS

In preparing for the ablation experiments, we conducted several preliminary proof-of-concept experiments to validate our test setup. Since R-LEMA will ultimately be performed in space, our tests attempted to minimize signal interference and the affects of our vacuum chamber. Experiments tested whether the FTIR spectrometer was in working order and ensured the vacuum chamber setup would not interfere with the spectra. We decided to test some common compounds with our setup and compare our data with the NIST Chemistry WebBook, which has a database of the spectra of many compounds.\(^3\) It is worth mentioning that our PbSe detector and KBr beam splitter combination only function to a minimum wavenumber of 2000 cm$^{-1}$, so any features below this wavenumber on the known spectra graphs are not shown on our graphs.
3.1 Isopropyl Alcohol

We placed a Petri dish containing isopropyl alcohol in the chamber and subsequently pumped it down. The alcohol evaporated in the low-pressure environment, forming a vapor within the chamber. We then took our spectra data to produce Figure 5a. The sharp peak at 3000 cm$^{-1}$ and the smaller bump near 3650 cm$^{-1}$ match those of the known spectra (Figure 5b).

![Figure 5](image)

(a) 99% Isopropyl was placed in a petri dish inside of vacuum chamber, and the low pressure vaporized solution into gaseous form, measured by the spectrometer. (b) An isopropanol spectrum from NIST Chemistry WebBook.3

3.2 Water

We placed a Petri dish containing water inside the vacuum chamber, and subsequently pumped it down. The low pressure was sufficient to evaporate a sizable fraction of the water, filling the chamber with water vapor. We then took data of absorption spectra, and produced the graph shown in Figure 6a. As one can see, it has a peak around 3400 cm$^{-1}$, which matches the known spectral graph for water vapor (Figure 6b). While the numerical absorbance values show poor agreement, this is not a concern because it only signifies that we had a lower density of water vapor present while taking the spectra compared to NIST Chemistry’s experiment.3

![Figure 6](image)

(a) Water spectrum measured in vacuum chamber; liquid water placed in a petri dish inside of vacuum chamber, and the low-pressure vaporized liquid water into gaseous form, measured by the spectrometer. (b) A water vapor spectrum from NIST Chemistry WebBook.3
3.3 Carbon Dioxide and Water (Breath)

We first pumped down the chamber to about 5 mTorr, and then exhaled into the vent inlet system of the chamber, simultaneously opening the valve to let the breath into the chamber. Immediately afterward, we took the spectra to obtain the graph shown in Figure 7a. There are peaks around 2350 cm\(^{-1}\) and 3700 cm\(^{-1}\), as well a broad peak at 3400 cm\(^{-1}\). Comparing with the known spectra graphs, we concluded that the 2350 cm\(^{-1}\) and 3700 cm\(^{-1}\) peaks belong to carbon dioxide (Figure 7b), and the broad 3400 cm\(^{-1}\) peak belongs to water (Figure 6b).

![Graphs showing breath spectrum and carbon dioxide spectrum](image)

Figure 7. (a) Breath spectrum measured through breathing in a pumped vacuum chamber, after the breath was held for two minutes. Note that this shows signs of water (Figure 6b) and carbon dioxide (Figure 7b) (b) a carbon dioxide spectrum from NIST Chemistry WebBook.

3.4 Preliminary Experiment Conclusion

Based on the similarities between our spectra graphs and known spectra, we concluded our FTIR machine was functioning and our vacuum chamber setup does not interfere with the process of taking spectra. We are hoping this setup can also be used in further experiments with negligible interference to the signal and spectra of our samples.
4. BASALT ABLATION EXPERIMENT

4.1 Baseline
Because actual asteroid samples were unavailable for analysis, future experiments will utilize samples of asteroid regolith simulant provided by NASA’s Kennedy Space Center Granular Mechanics and Regolith Operations Laboratory. In order to calibrate and verify the experimental setup, samples of basalt was used because FT-IR spectra of basalt (Figure 8) can be compared with those obtained by other researchers.4–6

Figure 8. IR spectrum of basalt obtained from ECOSTRESS Spectral Library6
4.2 Setup and Results

A basalt rock sample rested inside the vacuum chamber, which was pumped down to about 5 mTorr. A 150-W ablation laser (three 50-W lasers in tandem) enters the chamber through a quartz window and ablates the sample, ejecting a plume of gas from the basalt. While this occurs, the spectrometer sends an infrared beam through the ejected gas, collecting the spectra which is displayed in Figure 9.

![Absorbance plot](image)

Figure 9. A basalt sample was placed inside vacuum chamber. Lasers with a total power of 150 W at 808 nm were used to blast the target basalt; the resulting plume was measured by the spectrometer. During the process, vacuum pump was running and there are significant sparks coming from the rock by the ablation.

4.3 Analysis

The absorbance graph depicted for the basalt ablation is noisy, non-uniform, and does not seem to agree with the ECOSTRESS results in Figure 8. This could be due to sparks and blackbody radiation emitted by the basalt as it is ablated. At this point in our experiment, the signal to noise ratio is quite low and we are looking for ways to increase it. One proposed solution is to redirect a fraction of the output beam into a photodiode and then correct the overall spectra by accounting for the source’s fluctuating intensity. Looking beyond the noise, it seems that there are no distinct absorbance peaks for the measured basalt spectra. One possible explanation is the limited range of our PbSe detector. Our PbSe detector only functions in the range of wavenumbers between 2000 cm\(^{-1}\) and 7400 cm\(^{-1}\), and the main features of the basalt spectra may be beneath the wavenumber of 2000 cm\(^{-1}\), since silicon dioxide (a major component of basalt) is a heavier molecule and thus has a slower resonant frequency of vibration. In the future, the noise caused by sparking of the basalt rock will actually be our signal, as the black body radiation of the basalt sample will be the external source for our FTIR machine. This will ultimately limit the noise in measured spectra. A second spectrometer, the Bruker Vertex 80, will allow for use of an external IR source, being the radiation from our ablated black body sample, and conduct spectroscopy with this light source.
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