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# Miniature spatial heterodyne spectrometer for remote laser induced breakdown and Raman spectroscopy using Fresnel collection optics

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ABSTRACT

A combined laser induced breakdown (LIBS) and Raman, spatial heterodyne spectrometer (SHLS/SHRS) is described for remote measurements using Fresnel collection optics. The spatial heterodyne LIBS and Raman spectrometer (SHLS and SHRS) is based on a fixed diffraction grating interferometer with no moving parts that offers a very large field of view, high light throughput, and high spectral resolution in a small package. The field of view of the SHS spectrometer is ~1° making it very forgiving of collection optics alignment and image quality for remote LIBS and Raman measurements. In the SHLS/SHRS system described here, a ~100-mm diameter, f/1.25 Fresnel lens used for light collection is compared to a high quality ~100-mm aperture Questar long distance microscope. LIBS and Raman measurements were made at 10 m for a variety of organic and mineral samples including materials from deep ocean hydrothermal vents.

## 1. Introduction

The spatial heterodyne spectrometer (SHS) is an interferometer that has characteristics that are well suited for remote LIBS and Raman. Like other interferometers, the SHS has a very high light throughput and a wide field of view but also has very high spectral resolution. In addition, the SHS design has no moving parts making it compatible with a gated detector necessary for remote LIBS. The SHS, first described by Harlander [1,2], is similar to a Michelson interferometer but the interference pattern is formed on an imaging detector using stationary, rotated diffraction gratings, thus there are no moving parts. The grating rotation angle determines the Littrow wavelength, which is the wavelength about which all others are heterodyned. Heterodyning allows high spectral resolution to be achieved with a relatively small number of samples, fixed by the number of horizontal pixels on the imaging detector. The large entrance aperture and wide acceptance angle of the SHS provides high light throughput for extended sources, at least two orders of magnitude higher than a conventional dispersive spectrometer [1].

The first description of a laser based, gated SHS spectrometer was for visible Raman spectroscopy [3], and later for UV Raman [4,5] and remote Raman [5,6], and most recently for LIBS [7]. In the case of standoff LIBS and Raman, the wide acceptance angle and large aperture makes the SHS relatively easy to couple with telescopic optics and minimizes laser pointing stability issues, because small movements of the laser spot on the target do not reduce the amount of light collected by the spectrometer aperture, unlike the case of a dispersive spectrometer where the output of the telescope has to be held in focus on a narrow input slit [6]. In addition, all wavelengths are measured simultaneously in the SHS, making it compatible with pulsed lasers and gated detection, necessary in remote LIBS and Raman to reduce background.

The 2013 Planetary Decadal Survey recommends a high priority be placed on remote sensing technology with a focus on developing and maturing novel, crosscutting, low-mass/power sensors integrated into robust, low-cost system architectures [8]. Growing interest in the development of autonomous chemical measurement systems looks toward the CubeSat design. The CubeSat has a standard size and form factor; the smallest unit, 1 U, measures $10 \times 10 \times 10\ cm^3$ and weighs less than ten kilograms, and these units can be combined up to a 12 U size [9]. We are exploring remote Raman and LIBS instrumentation that might fit the CubeSat architecture. The SHS spectrometer and collection optics should ideally fit in a 1 U unit, however multiple units might be used for different components such as the laser, detector, and power supplies. In the case of Raman a small diode laser light source along with a small CMOS detector, similar to one we demonstrated recently in a cell-phone based SHRS spectrometer [10,11], might allow the entire spectrometer to fit a 1 U unit. Even in the case of LIBS, there are small pulsed lasers

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that are ideally suited to a 1 U architecture [12].

The SHS spectrometer design is ideal for small CubeSats because of the small size of the spectrometer. However, for remote spectroscopy large collection optics are required with short focal lengths to fit the 10 cm CubeSat dimensions (~f/1). Conventional f/1 lenses and mirrors are very thick and heavy and are not amendable. Large ~f/1 Fresnel optics on the other hand are very thin (e.g., 1–2 mm) and light weight. A Fresnel lens is a thin, flat piece of optical material having a series of grooves that approximate the spherical surface of a conventional lens. They are lightweight, cheap, and widely used for magnification and light collection, but image quality suffers due to increased scattering at the grooves [13]. Fresnel optics would seem to be ideal candidates as large aperture collectors in CubeSat remote spectrometers. Fresnel lenses have not been documented for the collection of Raman or LIBS spectra. In the following we describe a combined remote LIBS and Raman spatial heterodyne spectrometer, using Fresnel collection optics.

## 2. Experimental

For the continuous wave (CW) excitation Raman experiments, a frequency doubled 532 nm Nd:YAG laser (SpectraPhysics, Inc., Millenia Pro) was used to illuminate the sample. The beam diameter at the sample at 10 m is about 6–7 mm. Laser power was 93 mW for sulfur and 317 mW for potassium perchlorate. Acquisition times of 7 s for sulfur and 60 s for potassium perchlorate were used. For pulsed excitation, a Q-switched, frequency doubled Nd:YAG laser (Continuum Surelite III) was used to generate 532 nm laser pulses with a pulse width of 7 ns. The sample was illuminated from an angle of about 15° relative to the optical axis of the collection optics and spectrometer. The laser was operated at 1 Hz using 124 mJ/pulse for LIBS studies, and at 5 Hz using 24.9 mJ/pulse for Raman measurements. A beam expander (Newport Model HB-4XAR.14) was used to defocus the beam to ~10 mm on the sample for Raman measurements. For LIBS measurements the laser was focused to a small spot in order to form the LIBS plasma.

### 2.1. Spatial heterodyne spectrometer

The SHS interferometer consists of a 25 mm N-BK7 non polarizing 50:50 cube beamsplitter (Thorlabs BS013) and a pair of 150 grooves/mm, 25 mm square diffraction gratings blazed at 500 nm (Edmund optics #64–402). For Raman measurements, a 532 nm longpass filter (Semrock RazorEdge, LP03-532RE-25) and 600 nm shortpass filter (Thorlabs FES600) were used to remove strong Rayleigh scatter from the laser and to keep incoming signal within the SHS spectral range. An iris at the input aperture limited the size of the illuminated area on the gratings to 20 mm. For LIBS measurements, a 532 nm holographic notch filter (Kaiser Optical Systems, HSPF-532.0-2.0) was used instead of the 532 nm longpass filter. The interferogram was imaged onto the detector using a Nikon AF-S Nikkor 80–200 mm f/4.6G ED VRII lens (Nikon, Tokoyo, Japan) placed about 160 mm from the grating face on focal setting 105 mm. A spatial filter placed one focal length from the imaging lens was used to block higher grating orders. The detector was a thermoelectrically cooled 1024 × 253 gated ICCD array detector having 26 μm pixels (Princeton Instruments, Model PIMAX4). The ICCD gate width and delay time were optimized for each LIBS sample to give best interferogram quality as measured by the signal to background. Fourier transform of interferogram images was carried out in MATLAB to recover the spectrum. No apodization, flat field or instrument response corrections, or any other post processing were performed. Comparison LIBS spectra were measured using an Ocean Optics, LIBS-2000+ spectrometer with a 1064 nm laser. The sample chamber used 7, ~333 μm optical fibers for collection, placed approximately 25 mm from the surface of the sample (~f/75). Samples were excited with 200 mJ laser pulses at 1 Hz repetition rate, and 7.83 ns pulse width. The Q-switch delay was set to −20 us, where the negative sign means the Q-Switch is being fired before the aperture has opened. 100 shots with 2.1 ms integration time were averaged to produce the spectra.

### 2.2. Collection optics

Signal collection for standoff experiments used a two lens scheme, a 'collector' that collects light from the sample and a 'collimator' that collimates the collected light and sends it into the SHS spectrometer. The collimator lens also matches the beam size to the SHS spectrometer input aperture.

For these experiments, the collection efficiency of a 102 mm diameter, 1 mm thick acrylic Fresnel lens with focal length 127 mm (Knight Optical, LFG127102) was compared to that of a ~100-mm diameter Questar long distance microscope with 1300 mm effective focal length (Company Seven, Questar FR-1 MKIII model no. 33003/33024). A 25 mm diameter f/1 anti-reflection (AR) coated aspheric lens was used to collimate the collected signal into the SHS.

### 2.3. Samples measured

Sulfur (J.T. Baker) and Potassium perchlorate (Fisher Science) pellets were prepared using a die press. Calcite, quartz, gypsum, olivine, pyrite, barite, and malachite samples were obtained from an Introductory Earth Science Collection (American Educational, #1201–000). Mineral samples were washed in acetone prior to measurement. The hydrothermal vent samples and their elemental analysis were provided by Dr. Susan E. Humphris, Senior Scientist in the Geology and Geophysics Department at Woods Hole Oceanographic Institution.

## 3. Results and discussion

The SHS, depicted in Fig. 1A, is similar in construction to a Michelson interferometer with the mirrors replaced by stationary reflective diffraction gratings. The diffraction gratings are tilted such that one particular wavelength, the Littrow wavelength, is retro-reflected along the incident light path and recombines at the beamsplitter. The grating tilt, known as the Littrow angle, $\theta_L$, sets the heterodyned Littrow wavenumber, $\sigma_L$, that corresponds to zero spatial frequency according to Eq. (1), where $d$ is the diffraction grating groove spacing and $m$ is the grating order.

$$\theta_L = \sin^{-1}(m/2d\sigma_0) \quad (1)$$

For any wavelength other than Littrow, the diffracted light leaves the gratings at an angle to the optical axis, resulting in crossed wavefronts, inducing a spatial phase shift, and generating an interference pattern, which produces a series of wavelength dependent fringes on the array detector. The fringe frequency on the detector is given by Eq. (2), where $f$ is in fringes/cm and σ is the wavelength expressed in wavenumbers [14]. A Fourier transform of the interferogram recovers the spectrum. According to Eq. (2), emission lines above or below the Littrow wavelength show identical fringe patterns and can lead to degenerate lines (i.e., line overlap). This degeneracy can be removed by tilting one of the gratings vertically, which induces a rotation to the fringes, in opposite directions above and below Littrow [3]. In this case, a 2 dimensional (2D) Fourier transform can be used to recover spectra above and below the Littrow wavelength unambiguously. This is very useful to double the spectral range of the SHS.

$$f = 4(\sigma - \sigma_L)\tan\theta_L \quad (2)$$

The SHS, like other Fourier transform interferometers, does not require a narrow slit to achieve high resolution as is common with dispersive spectrometers because there is only a weak dependence of resolution on entrance aperture width. This allows the SHS to employ very large entrance apertures, greatly increasing the throughput of the system, which is advantageous when signal strength is low such as when the source is very far from the detector in a remote configuration.