OS21B-0205

Development of a Laser Raman Spectrometer for *In Situ* Measurements in the Deep Ocean

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Abstract

We have developed an ROV-deployable laser Raman spectrometer (LRS) to make in situ measurements of solid, liquid and gaseous species in the ocean (up to 4000 m depth). The LRS can be used to determine chemical and structural compositional information by irradiating the target with a laser and measuring the inelastically scattered (Raman shifted) light. The frequency shift from the exciting wavelength is due to characteristic molecular vibrations of the molecule; thus, the Raman spectrum serves as a fingerprint of a substance based on molecular composition and crystal structure. Raman spectroscopy is rapid, and typically requires no sample preparation. However, the weak Raman effect (~1 in 10^8 photons), the need for precise laser positioning, and fluorescence, pose challenges.

We have acquired an LRS from Kaiser Optical Systems, Inc. and adapted it for use in the ocean by dividing the components into three pressure cases, building penetrating fiber optic cables, developing an Ethernet interface to control the system from shipboard, and redesigning and rebuilding non-robust components. Future improvements will include weight/size reduction, adding through-the-lens visualization, and using liquid core optical waveguides to increase sensitivity. An increase in sensitivity of x10 may permit direct observation of natural seawater HCO_3 and CO_3 peaks.

The LRS has been successfully deployed over 6 times on MBARI's two remotely operated vehicles in 2002. Initial measurements of standards (e.g., isopropanol, calcite, and diamond) at depths as great as 3600 m have proven the effectiveness of the instrument in the deep ocean and have allowed us to advance methods for its use. Detailed spectra of seawater *in situ* and in the lab have also been obtained to better understand the ever-present seawater background (which includes water and SO_4 peaks, and very little fluorescence). We have used the LRS in a number of deep-sea CO_2 sequestration studies to acquire spectra of gaseous CO_2 and CO_2-N_2 mixtures from the surface to 400 m depth, and of liquid CO_2 and CO_2 hydrate on the seafloor at 3600 m. Future plans include measurements of gas vents, hydrothermal vent fluids and minerals, natural gas hydrates, sediment pore waters, and bacterial mats.

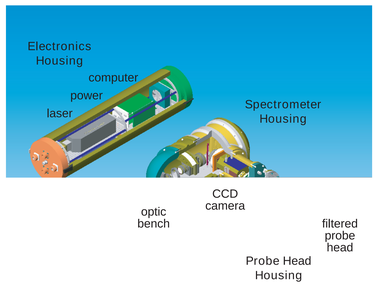

Figure 1.

In order to be operated in the deep ocean, the LRS was packaged into three pressure housings. The electronics housing holds the exciting laser, power inverter, and single board computer. The **spectrometer housing** holds the spectrometer, CCD camera, and associated electronics. The **probe head housing** contains only the probe head. The stand-off optic is used behind a thick dome window. The immersion optic protrudes through a flat titanium endcap with a gland seal. This housing is small enough to be deployed by the ROV manipulator.

The probe head is connected to both the laser in the electronics housing and the spectrometer via pressure jacketed fiber optic cables. The excitation fiber is 62.5 microns in diameter, and the collection fiber is 100 microns in diameter. Penetrators for the cables (to prevent losses associated with fiber optic connectors) were designed and built at MBARI.

Instrumentation

We acquired a HoloSpec f/1.8i laser Raman spectrometer (LRS) from Kaiser Optical Systems, Inc. (KOSI), including an Andor Technology 2048 x 512 CCD camera; a Coherent® DPSS 532 (Nd:YAG) green laser; and a Kaiser Mark II holographic filtered probe head with both a stand-off optic, and an immersion optic. The system was packaged for deep ocean (up to 4000 m depth) use as described in Figure 1. The LRS is connected to the ROV through a single cable that provides power and communications to the surface via Ethernet protocol. The instrument is controlled by a shipboard scientist with Kaiser's HoloGRAMS control software.

In addition to the high pressures, instruments deployed in the deep ocean are also subject to cold temperatures and a corrosive seawater environment. This created additional problems that needed to be addressed. Seawater leaks into a pressure housing are a distinct danger in deep ocean deployment. Temperature, humidity, and water sensors were installed in the electronics housing and the spectrometer housing to alert the user to leaks before serious damage is done. The change in temperature can affect the calibration of the instrument. Thus, knowing the temperature in the housings and being able to see how the instrument is affected are very important for properly analyzing the data.

Unlike in a laboratory environment, seagoing instruments are often subjected to significant jostling and vibrations. The instrument must also be removed from the pressure housings and taken apart often for inspection, repair and cleaning. For this reason, a few parts had to be removed and replaced with more robust components. These parts included the laser injector, and the slit optimization mechanism. In the case of the slit optimization mechanism, if the slit position changed when the instrument was in its pressure housing, nothing could be done to re-optimize it. Therefore, a motorized single-axis stage was installed such that slit optimization could be performed remotely. Prior to its installation, many measurements were made with the slit removed completely.

Calibration

The laser Raman spectrometer was calibrated prior to each deployment with Kaiser's HoloLab Series Calibration Accessory (HCA). The HCA uses a neon source for wavelength calibration, and a tungsten-halogen source for intensity calibration. A cyclohexane standard is used to check the laser wavelength. Spectra of standards (e.g., isopropanol and diamond) were obtained during deployment to verify the calibration. As noted above, changes in temperature can cause slight shifts in wavelengths. Therefore, a 0.5 mm thick, 2 x 2 mm diamond plate was installed in the beam path in the probe head. The sharp diamond peak at 1332 Δcm^{-1} provides an important reference point for observing any temperature-related wavelength shifts.

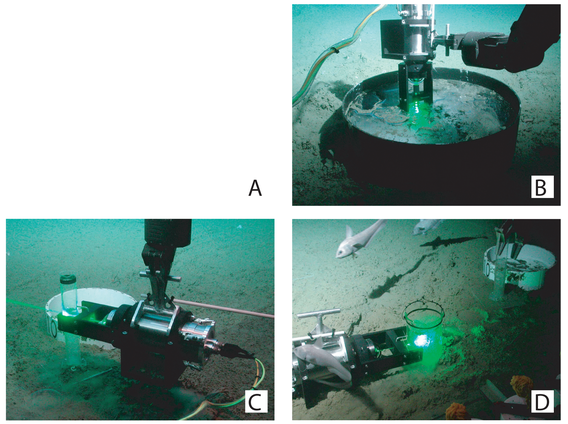

Figure 2.

The LRS deployed on the seafloor to obtain spectra from a range of targets (solids and liquids; gases had to be studied at shallower depths): **A)** Calcite at 663 m depth; **B)** liquid CO_2 pooled in a corral at 3607 m depth; **C)** CO_2 dissolved in seawater in a graduated cylinder at 3607 m depth; **D)** liquid CO_2 and CO_2 hydrate in a glass beaker at 3607 m depth.

The probe head is deployed by the manipulator (**B** and **C**). However, to isolate the probe head from vehicle and manipulator vibrations, the probe head was often off-loaded and positioned on the seafloor (**A** and **D**).

Operations

The LRS is deployed by a remotely operated vehicle (ROV). The electronics and spectrometer housings are mounted in the ROV toolsled, and the probe head is positioned at the target with the ROV manipulator (Figure 2). The exposure time is set by the scientist to obtain a strong signal while not saturating the CCD. Multiple accumulations are acquired and averaged to reduce noise in the spectra. Because the Raman effect is fairly small, excess light must be reduced. Therefore, during acquisition, the main ROV lights (which are HID and HMI lights) must be turned off. Secondary, incandescent lights are pointed away from the collection area. HMI and HID lights produce sharp peaks across the spectral region. Incandescent lights produce only a smooth background signal.

Focal Depth Issues

The most difficult aspect of using the LRS in the deep ocean is getting the target within the focal volume of the laser beam. The entire probe head or the target must be moved for focusing. For transparent objects (such as many liquids, gases, and solids such as calcite), the focal point of the beam can be fairly easily positioned inside of the target to obtain a good signal. For opaque objects, however, the surface must be positioned within the focal volume.

Two different objective lenses were used with the LRS; they will be referred to as the "immersion optic" and the "stand-off optic". Figure 3 defines the optical terms used to describe the objective lenses. The immersion optic has a very short focal length lens at the end of a 25 cm long tube with a pressure-tolerant sapphire window. This allows the optic to be place into a fluid stream for sampling. The working distance of the immersion optic is approximately 4 mm, and its depth of focus is ~0.2 mm in air (Figure 4). The stand-off optic has a focal length of 6.25 cm in air. For deep ocean deployments it must be used behind a dome pressure window which increases the focal length; the working distance (the distance from the dome window to the target) is 10 cm in water. The depth of focus is ~1 mm in air (Figure 4) and increases to ~3 mm in water. The laser spot size is on the order of tens of microns for both optics. The small spot size and the small depth of focus of both optics (~0.2-1.0 mm) requires precision positioning in order to be able to obtain spectra from opaque targets. This is beyond the capability of the ROV manipulator; therefore, a positioner with a precision of ~0.1 mm is being developed.

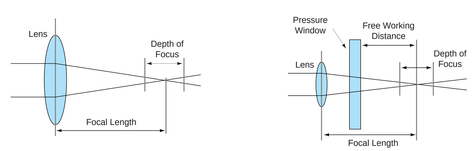

Figure 3.

Illustrations of optical terms: The **focal length** is the distance from the centerline of the lens to the point of focus. The **depth of focus** is the distance over which the target can be placed to obtain a signal strength of at least half of the maximum intensity (which is obtained at the point of focus-see Figure 4). If the lens is used behind a pressure window, the distance between the window and the point of focus is the **free working distance**.

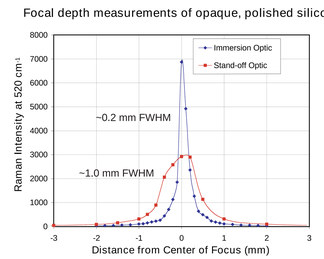

Figure 4.

The depth of focus of the LRS optics was determined by obtaining spectra from an opaque, polished silicon wafer. The depth of focus was taken to be the full width at half maximum of the peak (of the 520 cm^{-1} band of Si) on a plot of intensity versus distance from the sample. These measurements were performed in the lab, in air. Due to the effect of water on the optical path, the in-water depth of focus is slightly longer than the in-air depth.

The immersion probe, with a working distance of ~4 mm from the probe tip, has a depth of focus of ~0.2 mm. The stand-off optic has a depth of focus of ~1.0 mm. The immersion probe, therefore has a higher power density at the focus due to the smaller focal volume.

Seafloor Data

The LRS has been deployed eight times on both of MBARI's remotely operated vehicles (ROVs Ventana and Tiburon), and has collected data from solids, liquids, and gases in the deep ocean.

Liquids

Figure 5 shows spectra from two liquids: seawater at 400 m in the water column, and liquid CO_2 pooled on the seafloor at 3607 m depth. The Raman spectra of seawater (Figure 5A) is present as a background signal in most spectra obtained in the ocean. Therefore it is important to know its spectrum well. The characteristic peaks of water are the H-O-H bending mode near 1640 cm^{-1} (and its second harmonic at 3280 cm^{-1}), and the O-H stretching mode near 3450 cm^{-1}. Sulfate dissolved in seawater produces a peak at 981 cm^{-1}. At present, sulfate is the only dissolved species that the LRS is capable of detecting in seawater (28 mM). Enhancements and new techniques to improve the sensitivity of the instrument may enable us to measure dissolved HCO_3^-, CO_3, and CO_2 in seawater.

During studies of CO_2 sequestration, we have deposited small amounts of liquid CO_2 on the seafloor at depths of ~3600 m (see Figure 2B). CO_2 is a strong Raman scatterer and is characterized by a Fermi diad at ~1285 and ~1388 cm^{-1} (Figure 5B). The LRS allows direct measurements to be made of CO_2 as a liquid, a solid hydrate, and a gas to better understand how CO_2 behaves in the deep ocean.

Solids

Without the ability to position the LRS probe head precisely, we have only been able to obtain spectra of clear solids to date. Figure 6A shows the spectrum of a sample of calcite that was taken to the seafloor at 663 m (see Figure 2A). Calcite is characterized by peaks at 156, 282, 713, and 1086 cm^{-1}, which distinguish it from its polymorph aragonite. We were also able to obtain a spectrum from a diamond chip glued to a vial of isopropanol (taken down as a reference standard). The diamond peak at ~1332 cm^{-1} can be clearly seen in Figure 6B, superimposed over the isopropanol spectrum (with major peaks at 820, 953, and 1452 cm^{-1}).

Gases

We have used the LRS to obtain spectra of gases at shallow depths in the ocean, and to look at differences in dissolution rates of mixtures of gases. Figure 7 shows the spectra of a 50-50 mixture of CO_2 and N_2, and of pure N_2 gas. The calibration diamond was in place in the probe head; its peak can be seen at 1332 cm^{-1}. Gaseous CO_2 is characterized by the Fermi diad at ~1285 and ~1388 cm^{-1}; the band positions are upshifted with respect to those of liquid CO_2. N_2 has a single peak at 2331 cm^{-1}.

Future Work

The LRS is a useful *in situ* tool for studying a variety of processes in the deep ocean. Laser Raman spectroscopy is capable of discerning minerals prevalent at hydrothermal vent systems both in chimneys and as precipitates in the vent plume (e.g., anhydrite, sphalerite and pyrite - Pasteris, 1998). Increased sensitivity provided by enhancements such as liquid core optical fibers, should also allow measurements to be made of dissolved species in vent fluids (e.g., CO_2, CH_4, and H_2S). Laser Raman spectroscopy has also been used in the laboratory to study bacterial mats from Monterey Bay (Pasteris, et al., 2001). We would like to attempt similar experiments *in situ*. With the immersion optic, we can also penetrate into sediments to make measurements of pore water concentrations.

Laser Raman spectroscopy has become more popular as an *in situ* tool. A miniature version is being developed for use on a Mars rover (Wang, et al., 1998). A second-generation ocean LRS could be small enough to be used on a variety of platforms in the oceanographic community.

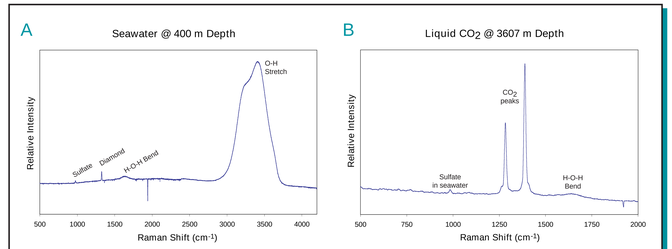

Figure 5.

Spectra of transparent liquid phases obtained on the seafloor with the LRS. **A)** Seawater at 400 m depth (using the LRS immersion optic). The characteristic peaks of water are the H-O-H bending mode near 1640 cm^{-1}, and the O-H stretching mode near 3450 cm^{-1}. Sulfate in seawater produces a peak at 981 cm^{-1}. The calibration diamond was in place and the peak can be seen at 1332 cm^{-1}. The dropout at ~1900 cm^{-1} is due to a dead spot on the CCD chip. **B)** A grapefruit-size blob of liquid CO_2 on seafloor (using the stand-off optic). CO_2 is characterized by the Fermi diad at ~1285 and ~1388 cm^{-1}. The 1640 cm^{-1} H-O-H bending mode of the seawater background can also be seen. (The calibration diamond was not in place for this spectrum).

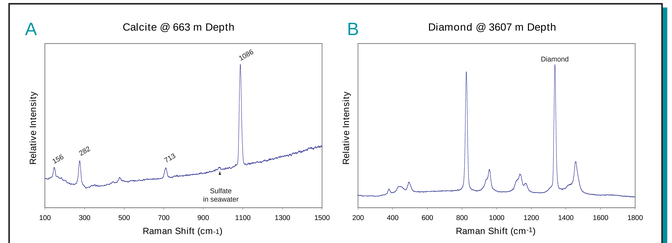

Figure 6.

Spectra of semi-transparent solid phases obtained on the seafloor with the LRS stand-off optic. **A)** Calcite at 663 m depth (see Figure 2A). Calcite is characterized by peaks at 156, 282, 713, and 1086 cm^{-1}. **B)** A diamond chip glued to a glass vial of isopropanol. The diamond peak is at 1332 cm^{-1}; all of the remaining peaks are from isopropanol.

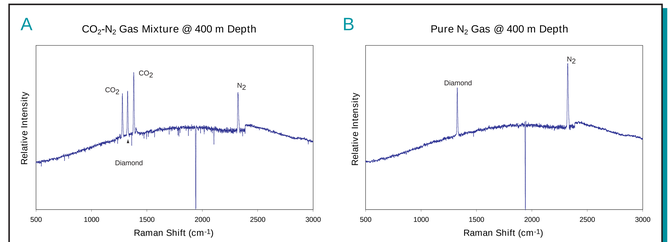

Figure 7.

Spectra of gaseous phases obtained at 400 m depth with the LRS immersion optic. **A)** A 50-50 mixture of CO_2 and N_2 gases. CO_2 is characterized by the Fermi diad at ~1285 and ~1388 cm^{-1}, and N_2 has a single peak at 2331 cm^{-1}. The calibration diamond was in place and the peak can be seen at 1332 cm^{-1}. **B)** Pure N_2 gas (2331 cm^{-1}) and the superimposed diamond peak (1332 cm^{-1}).

The step at ~2350 cm^{-1} is where the low lambda and high lambda regions were joined. The dropout at ~1900 cm^{-1} is due to a dead spot on the CCD chip.

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