Laser Raman Spectroscopic Instrumentation for *in situ* Geochemical Analyses in the Deep Ocean

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Abstract **- Engineers and scientists at the Monterey Bay Aquarium Research Institute (MBARI) have successfully developed instrumentation for performing laser Raman spectroscopy in the deep ocean. Laser Raman spectroscopy is a form of vibrational spectroscopy that is capable of performing rapid, non-destructive, *in situ* geochemical analyses. The Deep Ocean Raman In Situ Spectrometer (DORISS) is based on a laboratory model laser Raman spectrometer from Kaiser Optical Systems, Inc. The sample is interrogated by a 532 nm laser and the Raman backscattered radiation passes through a holographic grating and is recorded on a CCD camera. Laser Raman spectroscopy is capable of analyzing a variety of solid, liquid and gaseous species. Due to the strict requirements for positioning the laser focal point when analyzing opaque samples, a Precision Underwater Positioning (PUP) system was built to position the DORISS probe head with respect to the sample. PUP is capable of translating the DORISS probe head in 0.1 mm increments with 1 mm repeatability.**

DORISS and PUP are deployed by MBARI's remotely operated vehicles - ROVs *Tiburon* and *Ventana* - and are controlled by a scientist aboard the surface ship. DORISS and PUP have been deployed a number of times in Monterey Bay, the Gulf of California, and Hydrate Ridge, Oregon for testing and analyses of natural targets of interest. The development of smaller, second generation systems will allow DORISS and PUP to be carried on other deep submergence vehicles for use by the greater oceanographic community.

I. INTRODUCTION

Advancements in deep submergence technologies (e.g., remotely operated and autonomous underwater vehicles, and seafloor observatories) and new discoveries in the deep ocean have given rise to demands for new methods of *in situ* analyses. Acquiring data from deep sites without having to recover samples from every dive presents a new challenge to the technical oceanographic community. Many interesting science targets are not stable when removed from the pressure and temperature regime they are found in, such as high-temperature hydrothermal vent fluids and gas hydrates. In some cases, the goal is to observe a dynamic process and record the changes over time. Laser Raman spectroscopy is a technique capable of performing *in situ* geochemical analyses, which can analyze solid, liquid, and gaseous targets, as well as dynamic chemical processes in the deep ocean.

This paper will discuss the development, integration and successful deployments of a sea-going laser Raman spectrometer (DORISS – Deep Ocean Raman In Situ Spectrometer) and positioning system (PUP – Precision Underwater Positioner). DORISS/PUP have been deployed numerous times on MBARI's remotely operated vehicles (ROVs) *Tiburon* and *Ventana* (Fig. 1). Detailed specifications, design challenges, and science results are discussed along with future plans.

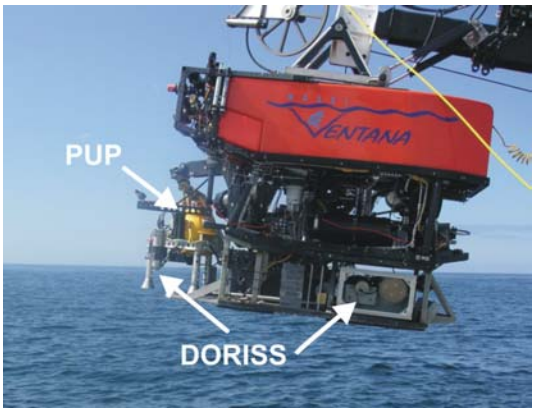

Fig. 1 – DORISS/PUP being deployed on the ROV *Ventana* in Monterey Bay

II. RAMAN SPECTROSCOPY

Raman spectroscopy is a form of vibrational spectroscopy based on Raman scattering – the inelastic scattering of monochromatic light from a target molecule [1]. An incident photon exchanges energy with the molecule and is scattered with lower or higher energy than the incident energy (Fig. 2). The change in energy is equal to the change in vibrational energy of the molecule. The Raman spectrum therefore

provides information about both the composition and the structure of the molecule.

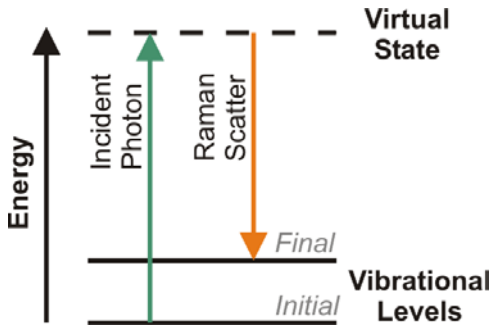

Fig. 2 – Energy level diagram of Raman scattering

Despite the fact that Raman scattering is a weak effect (only 1 in 10^8 photons are Raman scattered), it is a potentially powerful analytical tool for deep ocean geochemistry. Raman spectroscopy is rapid, non-destructive, and little to no sample preparation is required. Unlike IR spectroscopy, water does not cause major interference. The Raman spectrum of seawater consists of peaks from the bending and stretching of the water molecule, and a peak from the sulfate ion (Fig. 3). Most importantly, Raman spectroscopy is capable of analyzing solids, liquids, and gases.

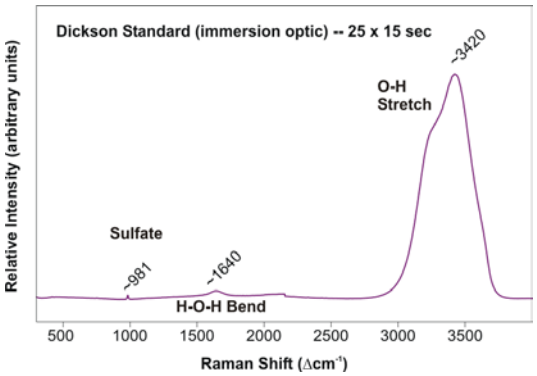

Fig. 3 – Raman spectrum of seawater [2]

A number of gases of interest to ocean scientists, such as carbon dioxide (CO_2), methane (CH_4), and higher hydrocarbons are Raman active [3,4]. They can be analyzed as gases, in dissolved form or incorporated in clathrates. Raman spectroscopy is capable of distinguishing between structure I, structure II and structure H hydrate by observing the partitioning of gases into the different lattice cages (large and small) [5,6]. For targets such as gas hydrates, which have stability zones confined to the deep ocean, it is highly advantageous to be able to analyze them *in situ*.

Minerals and other solid targets can also be analyzed *in situ* using Raman techniques. Sulfides, anhydrite, calcium carbonates, silicates, feldspars, magnetite, and hematite are just some of the substances that are easily identified [7,8]. This alleviates the need for an excessive number of samples to be brought to the surface for shore-based analysis, and allows for *in situ* mapping of mineral distribution.

III. DORISS DEVELOPMENT

Scientists and engineers at MBARI undertook the challenge of developing a laser Raman spectrometer (LRS) for use in the deep ocean [2,9]. Off-the-shelf technology was used to the fullest extent possible to prove the concept and manage risk. DORISS (Deep Ocean Raman In Situ Spectrometer) is based on a laboratory model LRS from Kaiser Optical Systems, Inc. (KOSI). The KOSI HoloProbe™ consists of a HoloSpec f/1.8i spectrometer with a duplex holographic grating, a 2048 x 512 charge coupled device (CCD) camera from Andor Technology, and a 532 nm Nd:YAG laser. The instrument was chosen for its resolution (~2-3 cm^{-1}) and spectral range (100-4400 cm^{-1}). The CCD camera selected has the option of being liquid cooled if the thermal conditions inside the pressure housing require additional cooling.

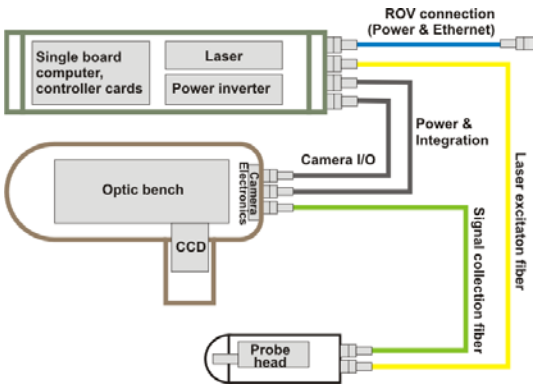

Fig. 4 - The conceptual configuration for the DORISS system

The instrument was divided into three pressure housings for use in the deep ocean to depths as great as 4000 m (Fig. 4). The electronics housing contains a single board computer, power components and the 100 mW 532 nm excitation laser (Fig. 5). Temperature and relative humidity sensors are present as well and are monitored continuously during a DORISS deployment. The housing is a glass filament reinforced epoxy construction that is slightly lighter and cheaper than a conventional aluminum or titanium design for the same 4000 meter depth rating. However, the reduced

thermal dissipation capability limits the power-on time when the outside temperature is above 27° C.

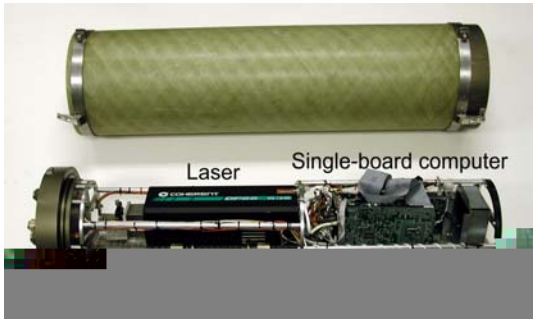

Fig. 5 – DORISS electrical housing and components [2]

The optical bench, CCD camera, and associated electronics are located in a separate housing (Fig. 6). The spectrometer housing was constructed of 7075 grade aluminum to minimize weight while taking advantage of the ocean's thermal capacity for cooling. To date additional liquid cooling of the CCD camera has not been required.

Fig. 6 - DORISS spectrometer housing and components [2]

The electronics housing (Fig. 5) and spectrometer housing (Fig. 6) are connected to each other with two cables providing power and communications between various components. These two housings are mounted in a drawer which is easily installed in the ROV toolsled (Fig. 1). A single connection to the ROV provides power and communications (Fig. 4).

The probe head housing contains the holographically filtered probe head which can accommodate a variety of sampling optics. The stand-off optic, as the name implies, allows the system to analyze a target without touching or entering the target material. The immersion optic is designed to be inserted into the target media. The stand-off optic is used behind a dome window, while the immersion optic protrudes from a flat endcap with a gland seal (Fig. 7). The off-the-shelf housing is constructed from 6AL-4V titanium and is small enough to be easily handled by the ROV manipulator. The probe head is connected to the laser and spectrometer via MBARI-built penetrating fiber optic cables.

Fig. 7 – Probe head with sampling optics and pressure housing [2]

Beyond packaging, additional modifications were required for the system to be used in the deep-sea environment. Adjustments easily made in a laboratory environment had to be automated for remote operations. The thumb-screw optimization mechanism for the spectrometer slit was replaced with a remote motor stage (Fig. 8). Custom shielded cabling was incorporated to keep the low level CCD camera signals from being degraded. As noted above, custom fiber optic penetrators were also designed and manufactured at MBARI to reduce signal loss and stay within time and budget resources allocated for the project.

Fig. 8 – Optical bench with slit motor stage (center), water sensor, and temperature and humidity sensor (bottom left)

Power and communications for DORISS also required some customization. The ROV *Ventana* distributes 110 VAC for payloads while the deeper diving ROV *Tiburon* offers 240 VDC. The DORISS system was modified to be capable of operating from either power source. The instrument is controlled by a ship-board scientist