Laser Raman Spectroscopy in the Deep Ocean

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Abstract

Laser Raman spectroscopy is a powerful tool for obtaining chemical and structural information from solids, liquids, and gases. It is a rapid, non-destructive technique which requires no sample preparation. Thus, it is well suited for making in situ measurements in the deep ocean.

We have modified a laser Raman spectrometer for use in the deep ocean. DORISS (Deep Ocean Raman In Situ Spectrometer) uses a 352 nm laser to excite a sample of interest and then records a spectrum of the Raman (inelastically) scattered light. The frequency shift of the Raman scattered light is due to characteristic molecular vibrations. The Raman spectrum serves as a kind of “fingerprint” of a substance based on both composition and structure. Raman spectroscopy can be used to study gases (e.g., CO2, CH4), liquids and dissolved species (e.g., CO2, SO2), in seawater, solids (e.g., precipitates, particles, minerals), and phase transitions (gas/liquid, and gas/solid are spectrally distinct).

We have successfully deployed DORISS to depths as great as 3600 m, and have obtained quality spectra from solid materials, liquids, and gases. Although we have primarily used DORISS for studies of CO2 sequestration and gas hydrates, it is applicable to a number of other fields: examples include mineralogy and fluid chemistry of hydrothermal systems, the CO2 system in the ocean, and bacterial mats.

The Raman Effect

Raman scattering is essentially the inelastic scattering of monochromatic radiation. An incident photon exchanges energy with the target molecule and is scattered with lower energy than the incident photon (Stokes) or higher energy than the incident photon (anti-Stokes scattering), respectively. An energy level diagram of the scattering is shown above. The observed energy shift of the scattered radiation is equal to the change in vibrational energy of the molecule, and is not dependent on the energy of the exciting radiation. It provides both compositional and structural information about the target. Thus, the Raman spectrum serves as a “molecular fingerprint.”

One of the big advantages of Raman spectroscopy is that it is capable of analyzing solids, liquids, and gases. It is rapid and requires little to no sample preparation, and is (generally) non-destructive. Although water itself is Raman active, the Raman spectrum of water is well known and does not obscure the signal of other target species.

Background image: DORISS’s 532 nm green laser illuminates a sample of natural gas hydrate collected at a gas vent in the Guaymas Basin during the 2003 Gulf of California Expedition.

Instrumentation

DORISS consists of a Kaiser Optical Systems HoloSpec f/1.8i spectrometer with holographic transmission grating and a 2048 x 512, front-illuminated Andor CCD camera. A 532 nm Nd:YAG laser and a Kaiser Mark II holographic filtered probe head. The components were divided into three pressure housings for use in the deep ocean (up to 4000 m depth). The system weighs ~450 lbs in air.

The electronics housing (at right) is a 10 inch diameter fiberglass housing with aluminum endcaps. It contains a single-board computer running embedded Windows NT with the CCD camera controller card, a power inverter, and the 200 W, 532 nm green excitation laser. Both the electronics and spectrometer housings have temperature, relative humidity, and water sensors.

The spectrometer, CCD camera, and camera electronics are housed in a custom-made aluminum housing (at left) with spherical endcaps and a side port to accommodate the spectrometer. A small power supply and remote linear stage controllers are mounted to the top of the optic bench. One of the linear stages is used to optimize the slit position when the spectrometer is sealed in its housing (the slit defines the resolution of the spectrometer).

The holographically filtered probe head is contained in a titanium housing (at right). A 2.5 inch stand-off optic is used behind a dome window. When the immersion optic is used, the dome window is replace by a flat endcap with a ground glass. The probe head is connected to the laser and the spectrometer by 7 m-long fiber optic cables, allowing it to be positioned by the ROV manipulator while the other housing remains mounted in the ROV towed vehicle.

Operations

The spectrometer and electronics housing are mounted in a towed vehicle which slides into the ROV towed vehicle as shown below left on ROV Tiburon. The probe head is carried in the front drawer or on the porch and is positioned by the ROV manipulator at the target of interest. The image below right shows the probe head positioned over a pool of liquid CO2 at 3607 m depth. While transparent targets are easy to analyze, positioning precision on the order of 0.1 mm is required when using the probe head to obtain spectra from opaque objects. An affordable precision underwater positioning (PUP) is being developed to provide this capability.

Although both IR and Raman are types of vibrational spectroscopy, the selection rules are quite different. Whether or not a molecule is Raman-active is dependent on the polarizability of the molecule.

Data

Laboratory Measurements

Spectra have been obtained using DORISS both in the lab and at sea. Because seawater is a background in most of our spectra, detailed analysis of the Raman signal of seawater was obtained in the lab using a Dickson standard. The seawater spectrum consists of a peak at ~3620 cm−1 due to the H2O-H bending mode, a peak at ~3981 cm−1 peak due to the O-H stretching of the water ion. Although other ions are present, they are either not Raman-active or have too low a concentration to be detected.

Labiory Measurements — Gases

During one of seven successful deployments in 2002, spectra were obtained of free gas confined to a open-bottomed box in which the immersion optic was inserted (thus no seawater background). A 50-50 CO2-N2 mixture was analyzed at 300 m depth and the change in concentration could be observed as CO2 preferentially dissolved into seawater. (A diamond plate in the probe head provided a 1332 nm calibration line. The drop-out at 1940 nm is due to a flaw on the CCD chip.)

Labiory Measurements — Liquids

During experiments on CO2 sequestration, we had the opportunity to obtain the Raman spectra of a blob of liquid CO2 on the seafloor at 3607 m depth. CO2 is characterized by the Fermi doublet — peaks at ~1285 and ~1328 cm−1 from the symmetric stretching and bending modes, respectively. A seawater background is observed as well by some fluorescent from the sediment on which the CO2 was deposited.

Field Test Measurements — Gases

To test the ability to analyze solids, a semi-transparent piece of calcite was taken to the seafloor at 663 m depth in Monterey Bay. As shown at right, calcite is characterized by peaks at 156, 282, 713, and 1066 cm−1 which distinguish it from its polymorph calcite. The H-O-H bending mode, a ~981 cm−1 peak, and the ~1640 cm−1 peak, due to the H-O-H bending mode, a ~981 cm−1 peak, and the ~1640 cm−1 peak.

Exploratory Field Measurements

During the Spring of 2003, the first measurements were obtained of a natural target — natural gas venting from the seafloor in Guaymas Basin. The spectrum showed the gas to be primarily methane with some additional minor constituents. Spectra of solid hydrates could not be obtained because precision positioning was not yet available.

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