Laser Raman Spectroscopy in the Deep Ocean

S. N. White (sheri@mbari.org), P. G. Brewer (brpe@mbari.org), E. T. Peltzer (etp3@mbari.org), W. Kirkwood (kiwi@mbari.org)
Monterey Bay Aquarium Research Institute, Moss Landing, CA 95039

Abstract

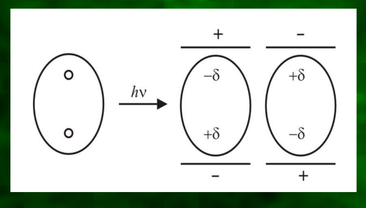
Laser Raman spectroscopy is a powerful tool for obtaining chemical and structural information from solids, liquids, and gases. It is a rapid, non-destructive technique which requires no sample preparation. Thus, it is well suited for making in situ measurements in the deep ocean.

We have modified a laser Raman spectrometer for use in the deep ocean. DORISS (Deep Ocean Raman In Situ Spectrometer) uses a 532 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 . So 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., CO_2, CH_4), liquids and dissolved species (e.g., CO_2 or SO_4^{2-} 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 minerals, liquids, and gases. Although we have primarily used DORISS for studies of CO_2 sequestration and gas hydrates, it is applicable to a number of other fields; examples include mineralogy and fluid chemistry of hydrothermal systems, the CO_2 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 or higher energy than the incident energy (Stokes and anti-Stokes scattering, respectively). An energy level diagram of Stokes 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."



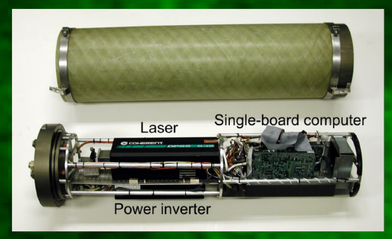
Although both IR and Raman are types of vibrational spectroscopy, the selection rules are quite different. Whether or not a molecule is Raman-active is dependent on the polarizability of the molecule.

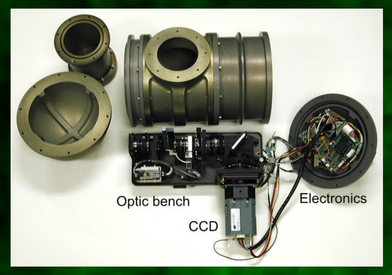
One of the big advantages of Raman spectroscopy is that it is capable of analyzing solids, liquids, and gases. It is rapid and requires little to no sample preparation, and is (generally) non-distructive. Although water itself is Raman active, the Raman spectrum of water is well known and does not obscure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

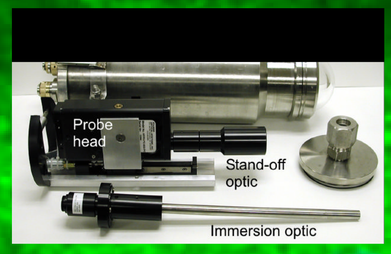
Background image: DORISS's 532 nm green laser illuminates a sample of natural gas hydrate collected at a gas vent in the Guaymas Basin during the 2003 Gulf of California Expedition.

Instrumentation

DORISS consists of a Kaiser Optical Systems HoloSpec f/1.8i spectrometer with holographic transmissive 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 weights ~450 lbs in air.

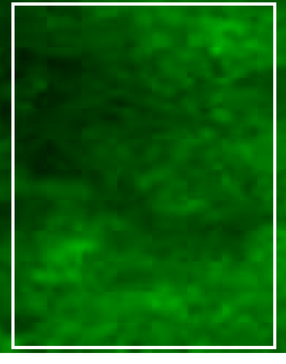


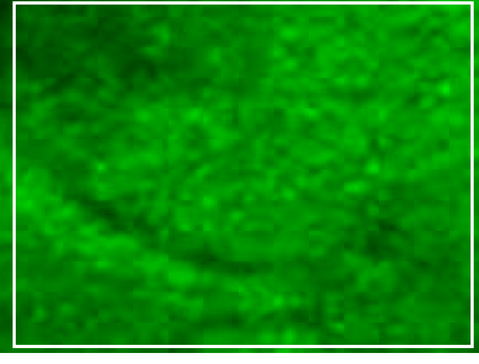




Operations

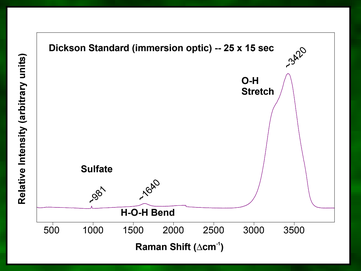
The spectrometer and electronics housings are mounted in a drawer which slides into the ROV toolsled (as shown below left on ROV Tiburon). The probe head is carried in the front drawer or on the porch and is positioned by the ROV manipulator at the target of interest. The image below at right shows the probe head positioned over a pool of liquid CO_2 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 off-loadable precision underwater positioner (PUP) is being developed to provide this capability.





Data

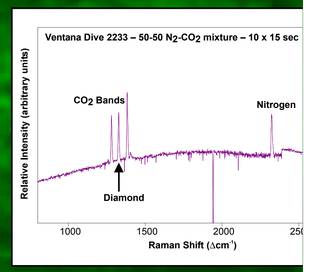
Laboratory Measurements



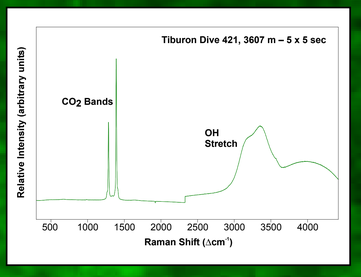
Spectra have been obtained using DORISS b the lab and at sea. Because seawater is a backgro most of our spectra, detailed analyses of the signal of seawater was obtained in the lab us Dickson standard. The seawater spectrum consi a peak at ~1640 Δcm^{-1} due to the H-O-H bending m peak at ~3420 Δcm^{-1} due to the symmetric stretching mode, and a ~981 Δcm^{-1} peak due to th stretch of the sulfate ion. Although other io present, they are either not Raman-active or ha low a concentration to be detected.

Field TestMeasurements — 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 CO_2-N_2 mixture was analyzed at 300 m depth and the change in concentration could be observed as CO_2 peferentially dissolved into seawater. (A diamond plate in the probe head provided a 1332 Δcm^{-1} calibration line. The drop-out at ~1940 Δcm^{-1} is due to a flaw on the CCD chip.)



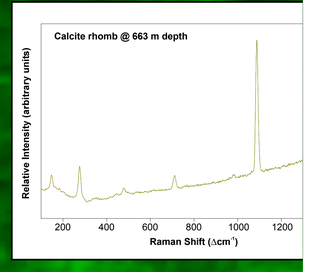
Liquids



During experiments on CO_2 sequestration, w the opportunity to obtain the Raman spectrum of of liquid CO_2 on the seafloor at 3607 m depth. characterized by the Fermi diad — peaks at ~128 ~1388 Δcm^{-1} from the symmetric stretch and be modes, respectively. A seawater backgrou observed as well as some fluorescence fro sediment on which the CO_2 was deposited.

Solids

To test the ability to analyze solids, a semi-transparent romb 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 1086 Δcm^{-1}, which distinguish it from its polymorph aragonite. It is harder to obtain spectra from opaque solids due to the stringent positioning requirements of the DORISS probe head as noted in the Operations section. We will attempt our first analyses of opaque targets in the summer of 2003 using the PUP.



Exploratory Field Measurements

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