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Portable remote Raman system for monitoring hydrocarbon, gas hydrates and explosives in the environment

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Abstract

We report our initial efforts to use a small portable Raman system for stand-off detection and identification of various types of organic chemicals including benzene, toluene, ethyl benzene and xylenes (BTEX). Both fiber-optic (FO) coupled and a directly coupled f/2.2 spectrograph with the telescope have been developed and tested. A frequency-doubled Nd:YAG pulsed laser (20 Hz, 532 nm, 35 mJ/pulse) is used as the excitation source. The operational range of the FO coupled Raman system was tested to 66 m, and the directly coupled system was tested to a distance of 120 m.

We have also measured remote Raman spectra of compressed methane gas and methane gas hydrate. The usefulness of the remote Raman system for identifying unknown compounds is demonstrated by measuring stand-off spectra of two plastic explosives, e.g. tri-amino tri-nitrobenzene (TATB) and beta-HMX at 10 m stand-off distance. The remote Raman system will be useful for terrestrial applications such as monitoring environmental pollution, in identifying unknown materials in public places in 10 s or less, and for detecting hydrocarbon plumes and gas hydrates on planetary surfaces such as Mars.

Keywords: Raman; Environmental pollution; Explosives; Gas hydrate; Hydrocarbons; Mars

1. Introduction

Hazardous waste has often been discarded into the environment from landfills and on industrial properties. Residual contamination from past fuel spills has created environmentally unacceptable conditions at several locations within the Hawaiian Islands, on the US Mainland, and around the world. Aviation gasoline spills pose additional concerns because of organic–lead additives (e.g. [1]). At one spill site on Oahu, HI (USA), it is estimated that ∼41,000 gal of gasoline have been floating over the groundwater (e.g. [2]). In addition to these hazardous agents, chemical agents can be released (gas or aerosols) into the atmosphere as a result of accidents or by terrorist activities. Identification of unknown materials in public places has, therefore, become increasingly important.

Recent discovery of methane (CH_4) in the Martian atmosphere by Mars Express has raised many questions about its origin. Is the methane detected in the Martian atmosphere abiogenic or biogenic, i.e., volcanic or produced by some other process? The answer to this question is presently not known, as no active volcano on Mars has been detected. If the early evolution of the Earth and Mars followed similar paths, then it is possible that methanogenic bacteria may have developed in the planet's early aqueous surface and near-surface environment [3]. During the transition of the early Martian hydrosphere to the colder conditions that characterize the planet today, such early life may have adapted to sub-permafrost conditions similar to the present deep biosphere environment of the Earth. The crust of Mars has been stable for a long time so that there is a possibility that methane, formed by magmatic processes and/or as a by-product of anaerobic deep biosphere activity, has risen toward the planet's surface. This methane would have been captured and stored as methane

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hydrate [4,5], which concentrates methane and water. There are two types of methane hydrates: (i) the type I CH_4 hydrate ($8CH_4 + 46H_2O$) and (ii) the type II CH_4 hydrate ($24CH_4 + 136H_2O$).

The Mars Odyssey Emission Imaging system (THEMIS) discovered water ice exposed near the edge of Mars' southern perennial polar cap [4]. Since CO_2 is the principal constituent of the thin atmosphere, it has been suggested that in the Martian subsurface along with CO_2-ice (also known as dry ice), CO_2 molecules may exist as gas hydrate ($8CO_2 + 44H_2O$) with melting temperature of 10 °C. The methane and carbon dioxide gas hydrates, if present, could have captured significant amounts of water on Mars.

Large deposits of hydrocarbon gas (mostly CH_4) hydrates that are largely biogenic in origin are found on the Earth's continental shelf at shallow depth. Natural gas generated in shallow ocean sediments to a depth of 300 ft mixes with thermogenic methane that may slowly seep from below. These gases form gas hydrates that are stable at shallow depths. The gas hydrate deposits can be 1000–2000 ft thick and cover large areas. Bands and lenses of gas hydrates are also found in the permafrost relatively close to the surface, e.g. Arctic deposits [6].

Various analytical techniques are being used for analyzing hydrocarbons in groundwater. Optical spectroscopy methods, especially Raman scattering, have been found suitable for this task (e.g. [7–10]). Telescopic Raman spectroscopy methods have been reported for stand-off detection of chemicals using both visible and UV laser excitation [11–17]. In this paper, we report our initial efforts to use a small portable Raman system for stand-off detection and identification of various types of chemicals including hydrocarbons, methane gas hydrates, dry ice and plastic explosives. Hydrocarbon benzene, toluene, ethyl benzene and xylenes isomers (BTEX) are present in gasoline. These BTEX compounds are ubiquitous contaminants in ground and surface waters. Because these compounds are known to be toxic to humans and aquatic life, their detection and identification is of critical importance.

2. Experimental methods

The experimental setup for our fiber-optic (FO) coupled stand-off pulsed Raman system for measuring spectra of organic compounds in the laboratory as well as outdoors is schematically shown in Fig. 1 and discussed in detail elsewhere [17]. In brief, this prototype Raman system consists of a telescope (Meade ETX-125 Maksutov-Cassegrain, 125 mm clear aperture, 1900 mm focal length, f/15), a frequency-doubled mini Nd:YAG laser source (Model ULTRA CFR, Big Sky Laser, 532 nm, 20 Hz), and an efficient (f/2.2) spectrograph (HoloSpec f/2.2, Kaiser Optical Systems Inc.) equipped with a gated intensified detector (Princeton Instruments Inc. Model I-MAX-1024-E). The maximum power of the laser at 532 nm is 35 mJ/pulse, the width of the laser pulse is approximately 8 ns, and the beam divergence is less than 0.8 mrad. Slits of 50 and 100 μm widths were used, respectively, for remote Raman measurements on gas hydrate and on liquid and vapor samples.

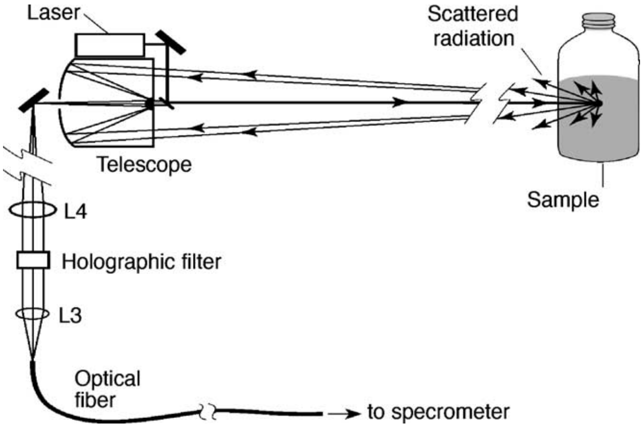

Fig. 1. Schematic diagram of a remote Raman receiver system showing fiber optic (FO) coupling of the telescope; L4, collimating lens and L3, focusing lens.

For evaluating the performance of the stand-off Raman systems, we used the following chemicals: Sigma–Aldrich: benzene (99.9%), toluene (99.8%), ethyl benzene (99%), xylene isomers (*o*-xylene (99%, HPLC grade), *m*-xylene (>99% anhydrous) and *p*-xylene (99% HPLC grade)), cyclohexane (99.8%) and dichloromethane (99%). Samples of 1 mol% pyridine in water and benzene vapors in equilibrium with benzene liquid at room temperature were also used for telescopic Raman measurements. For remote Raman measurements, high purity CH_4 gas was confined in a high-pressure optical cell and kept at a distance of 8 m from the telescope. Samples of methane gas hydrates were synthesized by Dr. Traci Sylva and Dr. Steve Masutani of Hawaii Natural Energy Institute and were examined with both micro-Raman and remote Raman techniques. Freshly made samples of gas hydrates were unloaded from the sample cell and transferred to a liquid nitrogen bath. Samples were sliced into small cylindrical shapes under liquid nitrogen. Raman spectra of selected hydrocarbons were also measured with a custom HoloPlex grating that simultaneously disperses the Raman spectra in the 80–2500 cm^{-1} and 2300–4400 cm^{-1} regions on the same CCD detector.

Raman spectra at a distance of 10 m from the telescope were obtained for all of the samples. For the stand-off Raman measurements, the liquid samples were contained in glass bottles 1.2 cm in diameter and 3 cm high. For remote Raman spectra of benzene at longer distances, the sample was contained in a square-bottom flask (5 cm × 5 cm; 100 ml, Kimax class A). The directly coupled remote Raman system was found to be 10 times more efficient than the fiber coupled system.