REMOTE-RAMAN AND MICRO-RAMAN STUDIES OF SOLID CO$_2$, CH$_4$ GAS HYDRATES AND ICE.
S. K. Sharma$^1$, A. K. Misra$^1$, P. G. Lucey$^1$, G. J. Exarhos$^2$, and C. F. Windisch, Jr.$^2$, $^1$Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI-96822. (sksharma@soest.hawaii.edu), $^2$Pacific Northwest National Laboratory, Richland, WA-99352.

Introduction: It is well known that on Mars CO$_2$ is the principal constituent of the thin atmosphere and on a seasonal basis CO$_2$ snow and frost coats the polar caps. Also over 25% of the Martian atmosphere freezes out and sublimes again each year [e. g., 1]. The Mars Odyssey Emission Imaging system (THEMIS) has discovered water ice exposed near the edge of Mars’ southern perennials cap [2].

In recent years, it has been suggested that in Martian subsurface CO$_2$ may exist as gas hydrate (8CO$_2$ + 44 H$_2$O) with melting temperature of 10°C. Since the crust of Mars has been stable for enough time there is also a possibility that methane formed by magmatic processes and/or as a byproduct of anaerobic deep biosphere activity to have raised toward the planet’s surface. This methane would have been captured and stored as methane hydrate [2, 5], which concentrates methane and water.

Determination of abundance and distribution of these ices on the surface and in the near surface are of fundamental importance for understanding Martian atmosphere, and for future exploration of Mars. In this work, we have evaluated feasibility of using remote Raman and micro-Raman spectroscopy as potential nondestructive and non-contact techniques for detecting solid CO$_2$, CH$_4$ gas, and gas hydrates as well as water-ice on planetary surfaces.

Equipment: (a) Remote Raman system: A pulsed remote Raman instrument is a modified version of an earlier instrument [6] developed at the University of Hawaii. The system consists of a 127 mm telescope (Meade ETX-125 Maksutov Cassegrain, 125 mm clear aperture, 1900 mm focal length), a frequency doubled mini Nd:YAG laser source (Model ULTRA CFR, Big Sky Laser, 532 nm, 35 mJ, 20 Hz), and a SPEX 500 M spectrometer equipped with liquid N$_2$ cooled CCD detector. The width of the laser pulses was approximately 8 ns, and the beam divergence was less than 0.8 mrad. Typical slit width for Raman spectral measurements was 100 –200 µm. Samples were placed at distance of 8 m from the telescope (limited by the space in the Laboratory). All remote Raman measurements with the SPEX spectrograph were carried out at the Pacific Northwest Laboratory, Richland, WA. It took a few hours in assembling the remote Raman system with portable UH telescope and laser system.

(b) Micro-Raman system. Details of micro-Raman system used for measurements at the University of Hawaii are described in detail elsewhere [7,8]. The Raman spectra of gas hydrate samples were recorded by placing the samples in random orientation on a microscope stage of a micro-Raman multichannel spectograph [8]. A 10X long-working (40 mm) distance objective (N.A. 2.2) focused 514.5 nm laser radiation from an argon ion laser in 180° scattering geometry on the sample. The laser power at the sample was 50 mW. A slit of 100 µm was used for all micro-Raman measurements reported here.

Samples: 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. A sample of dry ice at 8 m from the telescope was used for recording the remote Raman spectra of solid CO$_2$ in air at room temperature.

For micro-Raman measurements, samples of methane gas hydrates were synthesized by Dr. Traci Sylva and Dr. Steve Masutani of Hawaii Natural Energy Institute, and were provided for Raman investigations. 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.

Results and Discussion: Figure 1 depicts the Raman spectra of solid CO$_2$ and methane gas measured from a distance of 8 m. The spectra were collected with a 10 sec integration time and accumulated for 10 runs (total measurement time was 100 sec). As is evident from Fig. 1 we have very good signal to noise ratio in the spectra and the Raman lines are very sharp. In the spectrum of CO$_2$-ice (Fig. 1) the characteristic doublet due to Fermi resonance of internal modes of

![Figure 1. Portions of remote Raman spectra of solid CO$_2$ and of methane gas](1929.pdf)
vibration of CO$_2$ molecule is clearly visible. In the Raman spectrum of CO$_2$ gas characteristic Fermi doublet appears at 1286 and 1388 cm$^{-1}$. In the dry ice spectrum these sharp bands appear at 1278 and 1385 cm$^{-1}$. The frequencies of CO$_2$ doublet in the remote Raman spectrum are within experimental error of $\pm 1$ cm$^{-1}$ of the respective frequencies reported in the literature for the dry ice (e.g., [9]).

In the Raman spectra of methane gas the symmetric stretching mode, $\nu_1(A_1)$ of CH$_4$ give rise to strongest Raman band. At 1 atm and room temperature the $\nu_1$ mode appears at 2916.5 cm$^{-1}$ [10] and its frequency is found to increase in solid CH$_4$ with increasing pressure [11].

Raman spectra of methane hydrate at 77 K in the 2800-3500 cm$^{-1}$ region are shown in Fig. 2.

Figure 2. Raman spectra of synthetic gas hydrate in the 2800-3500 cm$^{-1}$ region showing the spectrum of the inner surface close to center of the core, and the outer surface of the sample.

In this figure (Fig. 2) we have compared the Raman spectra of two areas, (a) the inner surface close to center of the core and (b) outer surface. The inner surface of the sample clearly shows two additional peaks that correspond to formation of cubic sI structure of methane hydrate. The first large peak at 2900.4 cm$^{-1}$ (line width = 3.96 cm$^{-1}$) is methane trapped in the large cavity (5$^{12}$$6^2$) [12]. And the second peak at 2912.8 cm$^{-1}$ (line width = 4.38 cm$^{-1}$) indicates the existence of methane in the small cavity (5$^{12}$) [12]. The outer surface of the sample, however, shows only the ice signal.

According to the literature, the Raman peak positions corresponding to two cavities in structure sI of methane gas hydrates have values of 2915.04 cm$^{-1}$ (for 5$^{12}$ cavity) and 2904.85 cm$^{-1}$ (for 5$^{12}$$6^2$ cavity) [12]. These frequencies correspond to CH$_4$ hydrate sample near 0° C. Our data indicates that as the samples are cooled to lower temperature of 77 K (-196° C), there is a shift in the position of the Raman bands of methane hydrates. The other broad Raman peaks at 3085.5 cm$^{-1}$ (width 27.4 cm$^{-1}$), 3209.7 cm$^{-1}$ (width 46.6 cm$^{-1}$), 3318.1 cm$^{-1}$ (width 172 cm$^{-1}$), 3410 cm$^{-1}$ (width 68 cm$^{-1}$) are the fingerprints of stretching Raman modes of H$_2$O molecule. The strong O-H symmetrical stretching mode of ice has been shown [13] to shift towards lower frequency upon cooling because of change in hydrogen bonding.

These experiments on dry ice, methane gas, bulk CH$_4$ gas hydrate and ice demonstrate that it should be feasible to detect and differentiate between various types of ices with laser Raman spectroscopy. Miniaturization of both micro- and remote Raman spectroscopic instruments, and recent use of fiber optic based Raman system for in situ measurements in the deep ocean [14] clearly show that both remote Raman and fiber-optic based systems with suitable modifications can be used for detecting gas hydrates on the planetary surfaces, and also on Earth in sediment cores and boreholes as well as on the sea floor.

Acknowledgments: This work has been supported in part by US DOE via Battelle Memorial Institute Pacific Northwest Division, and by NASA under a PIDDP grant NAG 5-13101.