

DETECTION OF WATER AND WATER BEARING MINERALS FROM 10 M DISTANCE UNDER BRIGHT CONDITION USING REMOTE RAMAN SYSTEM. A. K. Misra¹, S. K. Sharma¹, Chi Hong Chio², P. G. Lucey¹, ¹Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii, 2525 Correa Rd. HIGP, Honolulu, HI 96822, USA; (anupam@hawaii.edu); ²Department of Chemistry, Univ. of Hawaii, Honolulu, HI 96822, USA.

Overview: Detection of water and carbon is important in order to support existence of life on other planets. Water has been detected on Mars and Moon in the form of ice and in hydrous minerals. Among the various techniques to detect water, ice, and H₂O/OH bearing minerals, Raman spectroscopy stands out as providing distinctive spectra for unambiguous identification of water and water bearing minerals. A portable remote Raman instrument developed at the University of Hawaii has been shown earlier to detect carbon in carbonate form in calcite, magnesite, dolomite, siderite etc. from distances of several meters in matter of seconds [1-3]. The Remote Raman system is shown here to detect water, ice, and water bearing minerals from a distance of 10 m under bright conditions with short integration time. The ability to detect water and other minerals from remote distances during daytime would be promising for analyzing targets at hard to reach places such as lakes, cliffs, craters etc.

Introduction: Recently a portable remote Raman system developed at the University of Hawaii has been tested to obtain Raman spectra of minerals and organics from distances ranging from 10 to 100 m in daylight condition [1-2]. Minerals with various functional groups such as carbonate, oxides, silicates, sulfates, nitrates and phosphates were identified from the Raman spectra acquired with a single laser pulse excitation [3]. The single shot-spectra collected under illuminated condition and 1 μ s integration time, show clear Raman features. In order to measure Raman spectra in daylight or under a well illuminated background, it is important to use a pulse laser source and a gated detector [1-3]. Such a combination significantly improves the signal to background ratio of the Raman peaks which have very weak cross-sections in comparison to Rayleigh or Mie scattering cross-section. Gated system also helps in reducing long-lived fluorescent background generated by inorganic fluorescent impurities, e.g., transition ions and rare-earth ions [4-7]. Raman spectra of water, ice, and various water bearing minerals such as gypsum (CaSO₄·2H₂O), chalcantite (CuSO₄·5H₂O), bischofite (MgCl₂·6H₂O), epsomite (MgSO₄·7H₂O), melanterite (FeSO₄·7H₂O), rozenite (FeSO₄·4H₂O), szomolnokite (FeSO₄·1H₂O), sinjarite (CaCl₂·2H₂O), and hydrous sodium phosphates NaH₂PO₄·2H₂O, Na₃PO₄·12H₂O were measured from a 10 m distance in a well illuminated lab. The

presence of water could be easily detected in all the sample through their Raman spectra.

Experimental Set-up and Samples: The pulsed remote Raman system has been described in detail elsewhere [1-3,8]. In brief it consists of a 127-mm telescope (Meade ETX-125 Maksutov cassegrain, 1900 mm focal length), a frequency-doubled mini Nd:YAG pulsed laser source (model Ultra CFR, Big Sky Laser, 532 nm, 24 mJ/pulse, 20 Hz, pulse width 8 ns, central laser spot divergence 0.8 mrad), a Kaiser F/1.8 HoloSpec spectrometer equipped with a gated thermo-electrically cooled CCD detector. The telescope is directly coupled to the spectrometer through a 20x (NA = 0.35, long focal length = 20 mm) microscope lens. A 532 nm SuperNotch Plus holographic filter is used in front of the microscope lens to minimize the Rayleigh scattering signal from the target. Raman spectra were measured in a coaxial mode where the laser is made coaxial with the telescope optical axis using two prisms. All spectra were measured using a 100 micron slit with the intensified CCD in the gated mode in the lab with all lights turned on. Samples were placed 10 m away from the telescope. Spectra were measured with integration time of 1, 10 and 30 s in gated mode with gate width of 2 μ s. No cosmic ray or baseline corrections were applied to the spectra presented here.

Neon lines were used in calibrating the spectra and measured Raman spectra of benzene and cyclohexane verified peak positions within ± 2 cm⁻¹ of standard values obtained from the NIST website [9].

The rock-forming mineral samples (gypsum, anhydrite etc.) were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. These samples were used without any polishing or cutting. Water bearing compounds were analytical grade chemicals in the powder/bulk form from Fisher Scientific, USA. Water sample was from drinking tap water.

Results: Figure 1 shows remote Raman spectra of water, ice, NaH₂PO₄·2H₂O, and FeSO₄·7H₂O in low frequency region, 30 to 2400 cm⁻¹, from a distance of 10 m with integration time of 10 s. In the spectrum of water, the low frequency Raman band at 182 cm⁻¹ is due to lattice vibrations associated with the intermolecular stretch. The bending mode (ν_2) of water molecule is observed as a broad band near 1645 cm⁻¹. The strong peak at 911 cm⁻¹ in the NaH₂PO₄·2H₂O spectra corresponds to symmetrical stretching modes of phos-

phate ions ($\nu_1(\text{PO}_4^{3-})$). The symmetrical stretching modes of sulfate ions ($\nu_1(\text{SO}_4^{2-})$) in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is observed at 977 cm^{-1} .

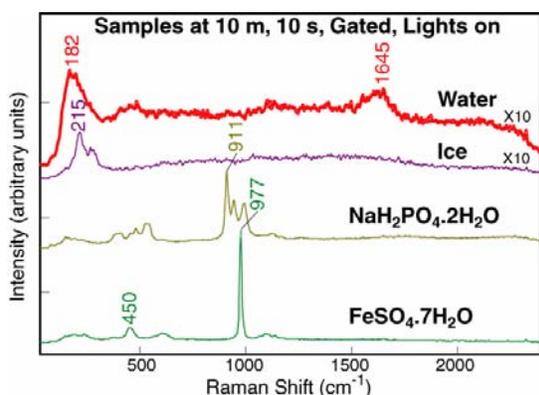


Fig. 1: Remote Raman spectra of water, ice and selected water bearing minerals in the low frequency region showing Raman bands corresponding to the quasi-lattice (182 cm^{-1}) and bending mode (1645 cm^{-1}) of water. The symmetric stretching modes of phosphate and sulfate ions are observed at 911 and 977 cm^{-1} respectively.

Figure 2 shows the Raman spectra in the high frequency region (2400 to 4500 cm^{-1}) of water, ice, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Water gives very

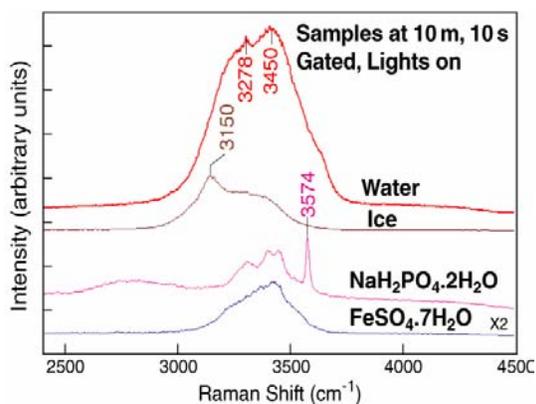


Figure 2: Remote Raman spectra of water, ice and water bearing minerals in the high frequency region showing Raman bands corresponding to the stretching mode of water.

strong Raman signal in the $3100 - 3600 \text{ cm}^{-1}$ spectral region, and it is easy to detect water in various forms even with integration time of 1 s . The spectra shown here were obtained from samples placed at 10 m distances with all lab lights on and 10 s integration times.

Raman spectra these samples can also be obtained with 1 s integration time.

In liquid water, strong broad Raman bands at 3278 and 3450 cm^{-1} are the symmetric (ν_1) and antisymmetric stretching (ν_3) vibrational modes of the water molecule, respectively. The stretching modes of vibrations usually produce the strongest Raman signals. Ice can be distinguished from liquid water by the presence of a sharper band at 3150 cm^{-1} . Very sharp and strong bands near 3500 cm^{-1} in Raman spectra of hydrous minerals indicate the stretching modes of a chemically bonded water molecule. In the spectra of $\text{NaH}_2(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ the peak at 3574 cm^{-1} represents the asymmetric stretching mode of water molecule. The chemically bonded water molecules in gypsum are observed at 3405 cm^{-1} and 3493 cm^{-1} . Because of the chemical bonding of water with the minerals, water molecules can exist in these minerals at temperatures significantly above the boiling point of liquid water. The remote Raman system would be able to easily detect chemically bonded water molecules in minerals lying in the dry environment which otherwise show no evidence of liquid water.

Summary: The data presented show the ability of a portable remote Raman system to detect water, ice and water bearing minerals from a distance of 10 meters in a well illuminated background. Such system would be ideal for identifying minerals and searching for water on a planetary surface during daylight.

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