A PORTABLE REMOTE RAMAN SYSTEM FOR DETECTION OF MINERALS, HYDRATED SULFATES, WATER/ICE AND ORGANICS FOR PLANETARY EXPLORATION MISSIONS. Y. Q. Xin, H. K. Qu, Z. C. Ling, Shandong Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China (yqxin@sdu.edu.cn, zcling@sdu.edu.cn).

Introduction: Raman spectroscopy is known as an efficient non-destructive spectroscopic technique for detection of molecular structure that has been applied to mineralogy, gemology, planetary mineral analysis and space exploration, astrobiology and biomineralization, cultural heritage and archaeometry, etc. Many outstanding and attractive scientific outputs of returned extraterrestrial samples, meteorites and planetary analogues have been reported since Raman spectroscopy is used to the field of planetary science [1, 2]. More importantly, as the great ability of detection of water, ice, organics, H<sub>2</sub>O/OH minerals and gases, a few planetary scientific teams have proposed that Raman spectrometer should be one of the payloads for future Mars, Moon, Venus and asteroids missions.

Remote Raman spectroscopy which is able to detect at a distance of several meters to hundreds of meters is considered to have wide applications in the field of planetary explorations for detecting ice/H<sub>2</sub>O (e.g. polar regions of Moon and Mars), identifying the minerals, determining gas molecules, and even searching for signs of life [3-5]. ESA and NASA have planned to launch Raman payloads on the first Mars missions in 2020. Raman Laser Spectrometer (RLS) on board the ESA/Roscosmos ExoMars 2020 mission will be employed to obtain in-situ spectra of Martian surface/subsurface minerals [6]. The Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals (SHERLOC), a Deep UV resonance Raman and fluorescence spectrometer with a 248.6-nm laser, will be mounted on the arm of Mars 2020 rover mission [7]. Furthermore, a remote Raman integrated in SuperCam with 532 nm laser is aboard NASA's Mars 2020 rover for determining mineralogy at a distance of 12 m [8].

**Experimental Facility:** In this work, we built a remote Raman system in Shandong University (Weihai) using a compact Nd:YAG Q-switched laser source (Beamtech Optronics Co, Ltd Dawa-200 Laser, 1064 nm,  $0\sim232$  mJ/pulse,  $0\sim20$  Hz, pulse width 9 ns, central laser spot divergence ~1 mrad, diameter ~6 mm), a spectrograph equipped with a thermoelectrically cooled charge-coupled device (CCD) detector, and a telescope (ELESTRON NexStar 6SE, 150 mm diameter, 1500 mm focus length) as shown in Fig. 1. The spectrograph contains two volume phases holographic grisms and its spectral resolutions for a 50 µm silt is 5.48 cm<sup>-1</sup> in 531-614 nm and 4.8 cm<sup>-1</sup> 605-699 nm. The 532 nm green laser used in an oblique geometry to excite Raman

signals is generated by second harmonic generation of 1064 nm laser with a frequency doubling crystal KTP ( $8 \times 8 \times 8$  mm) whose exchange efficiency is around 45-50%. The power of laser at 532 nm is about 45 mJ/pulse. Laser spot diameter on samples is about 1.5 cm at a distance of 4 m. Raman signal is collected by the telescope and focused on a fiber probe by a convex lens. The 532-nm laser reflected is removed by a 532 nm Notch filter fixed in the spectrometer. All samples are fixed in the front of telescope at a distance of 4 m. A commercially available software GRAMS<sup>TM</sup> was employed for spectral analysis.

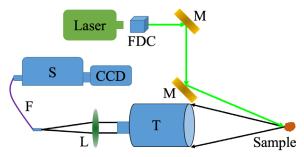


Fig. 1. Schematic diagram of the remote Raman system. M = Mirror, FDC = Frequency Doubling Crystal, S =Spectroscopy, F = Fiber, L = Lens, NF = 532nm Notch Filter, T = Telescope.

## **Results and Discussion:**

The Raman spectra of  $KNO_3$ ,  $K_2CO_3$ ,  $H_2O$ , ice, olivine, plagioclase, K-feldspar, hydrated sulfates and organics are acquired via the remote Raman system.

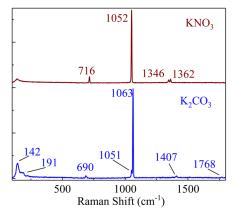


Fig. 2. Remote Raman spectra of  $KNO_3$  and  $K_2CO_3$  with 10 s exposure time.

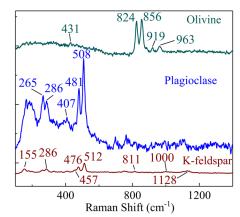


Fig. 3. Remote Raman spectra of olivine, plagioclase and K-feldspar with 40, 30 and 20 s exposure time, respectively.

Raman spectra of KNO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> with a goodquality signal to noise ratio (SNR) is shown in Fig. 2. The diagnosed Raman peaks around 824 and 856 cm<sup>-1</sup> which are attributed to  $v_1$ - and  $v_3$ -derived vibrational modes of SiO<sub>4</sub> are the Raman fingerprint features of olivine (Fig. 3). Plagioclase and K-feldspar also can be distinguished from their Raman spectra.

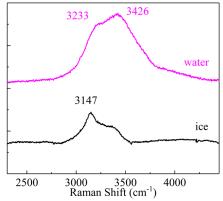


Fig. 4. Remote Raman spectra of water and ice with 20, and 30 s exposure time.

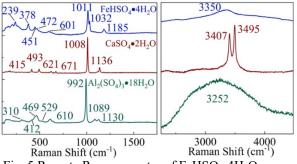


Fig. 5 Remote Raman spectra of FeHSO<sub>4</sub>·4H<sub>2</sub>O, CaSO<sub>4</sub>·2H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O with 30, 20 and 20 s exposure time.

Hydrated minerals, as the host of water, are significant for planetary exploration missions. Three

species of hydrated sulfates which may exist on Mars or other plants are selected as experimental samples. It is distinguishable to identify mineral phases with characteristic Raman spectra (Fig. 5). As one of the possible evidences of extraterrestrial life, water/water ice is always a crucial target for planetary exploration missions. Raman peaks of liquid water around 3233 and 3426 cm<sup>-1</sup> are assigned to  $v_1$  and  $v_3$  vibrational modes of water molecule. Raman spectra of ice exhibits a sharper peak at 3147 cm<sup>-1</sup> due to H-O-H symmetric stretching mode (Fig. 4). Furthermore, Raman spectra of phenylalanine as organics exhibits distinct peak around 1004 cm<sup>-1</sup>, entirely different from inorganic mineral phases (Fig. 6). The unique fingerprint spectra can provide direct identification of mineral phases for future planetary missions.

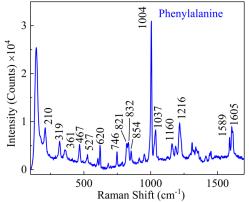


Fig. 6 Remote Raman spectra of phenylalanine with 5 s exposure time.

Acknowledgments: This work is supported by the Pre-research project on Civil Aerospace Technologies No. D020102 funded by China National Space Administration (CNSA). We also thank the fundings from the National Natural Science Foundation (11941001, 41972322, U1931211), the Natural Science Foundation of Shandong Province (ZR2019MD008), Qilu (Tang) Young Scholars Program of Shandong University, Weihai (2015WHWLJH14). This work is also supported by Physical-Chemical Materials Analytical & Testing Center of Shandong University at Weihai.

**References:** [1] Ling Z. C. and Wang D. (2010) *Icarus, 209,* 422–433. [2] Wang A. et al. (1999) *JGR planets, 104,* 8509-8519. [3] Sharma S. K. et al. (2010), *SPIE, 7691,* 76910F. [4] Sharma S. K. et al. (2011), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 01,* 75-81. [5] Sharma S. K. et al. (2006), *Appl. spectroscopy, 60,* 871-876. [6] Rull F. et al. (2017) *Astrobiology, 17,* 627-654. [7] Beegle L. W. et al. (2014) *AGU Fall meeting,* Abstract #2162. [8] Wiens R. C. et al. (2017) *Spec, 32,* (LA-UR-17-26876).