

REMOTE RAMAN MEASUREMENTS OF MINERALS, ORGANICS AND INORGANICS AT 430 M RANGE. T. E. Acosta-Maedar¹, A. K. Misra¹, S. K. Sharma¹, G. Berlanga¹, D. Muchow¹ and L. Muzangwa¹
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Introduction: Remote Raman has been demonstrated as a viable technique for planetary exploration. Raman spectroscopy requires no sample preparation and can provide univocal chemical characterization without sample damage. Remote Raman systems fitted with gated lasers and detectors can perform fast measurements under daylight at increasing distances. Larger measurement ranges increase the effective exploring area of a planetary rover, saving mission time and increasing the number of accessible targets. The University of Hawaii (UH) has developed multiple Remote Raman systems. The system used for this study can perform measurements of organics and inorganic chemicals such as benzene or calcite at 120 meters range [1]. In this study we report the ability of the Remote Raman system to perform good quality fast measurements up to 430 m range. UH is collaborating with LANL and french partners VIRAP and CNES under the Mars 2020 mission in which the SuperCam instrument will perform Remote Raman analysis of Mars rocks, along with LIBS and time-resolved fluorescence [2].

Experimental setup: Figure 1 shows the Remote Raman system in the UH Manoa campus, with the target samples placed in a balcony at 430 meter range. The system is gated with coaxial geometry. The collection is made through an 8-inch (203.2 mm) diameter telescope (Meade LX-200R Advanced Ritchey-Chretien, f/10). The sample is excited with a frequency-doubled Q-switched Nd:YAG pulsed laser source (Quantel Laser, CFR model, 532 nm, 100 mJ/pulse, 15 Hz, pulse width 10 ns). The system is fitted with a Kaiser Optical Systems f/1.8 HoloSpec spectrometer equipped with a 1024x256 intensified CCD camera (PI-IMAX, Princeton Instrument, Trenton, NJ). The telescope is directly coupled to the spectrometer through a camera lens. A 532-nm notch filter is used to remove the laser light. The system is mounted on a pan-and-tilt scanner allowing to accurately aim the system at large distances. The laser was focused on the sample through a 10x beam expander mounted in front of the laser. We focused it to obtain a parallel beam and a laser spot 10 cm in diameter at 430 meter.

We successfully measured acetone, benzene, cyclohexane, dry ice, gypsum, potassium chlorate, potassium perchlorate, potassium nitrate, ammonium nitrate, marble rock, methanol, quartz, sulfur, urea, water and water ice, acetonitrile, anhydrite, and magnesium sulfate with integration times of 10 s or less. Liquid sam-

ples were placed in large vials and powdered samples were placed inside 4 inch diameter petri dishes.

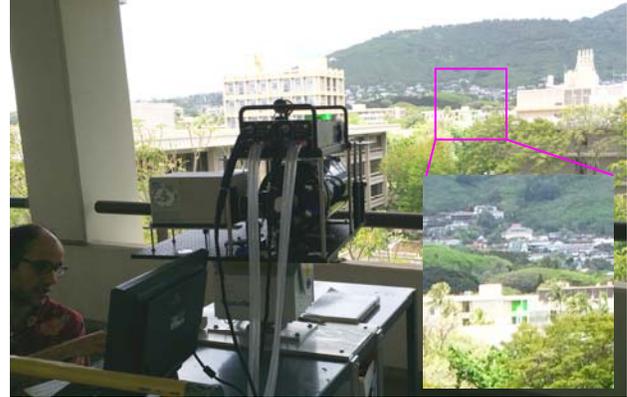


Figure 1: experimental setup showing the Remote Raman instrument and, in the enlargement, the target sample location 430 m away.

Results and Discussion: Figure 2 shows the remote Raman spectra of ammonium nitrate (NH_4NO_3), potassium nitrate (KNO_3), potassium chlorate (KClO_3) and urea ($\text{CO}(\text{NH}_2)_2$) with fast 1 second integration time, equivalent to 15 laser pulses. In the potassium nitrate spectrum, the 1052 cm^{-1} peak corresponds to the symmetric stretching vibrations ν_1 in the nitrate ions NO_3^- . The 1349 cm^{-1} peak corresponds to the ν_3 mode. The NH_4NO_3 and KNO_3 molecules both contain NO_3^- ions, and the 1044 , 1288 , and 1655 cm^{-1} Raman

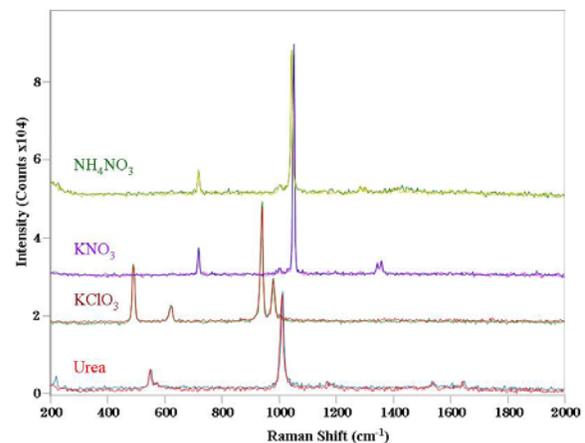


Figure 2: Remote Raman spectra of NH_4NO_3 , KNO_3 , KClO_3 , and urea at 430 m range with 1 s detection time. Two consecutive spectra are shown for each sample to demonstrate repeatability.

vibrational modes of NH_4NO_3 are analogous to the 1052 , 1349 , and 1664 cm^{-1} peaks in KNO_3 . The multi-

peaks between 1400 and 1500 cm^{-1} are the result of vibrational coupling between some ammonium ion deformation and nitrate stretching. Similarly urea and potassium chlorate show distinct Raman peaks that allow unequivocal chemical identification at 430 meter range and 1 second integration time. Urea peaks are found at 1002 cm^{-1} as well as at 1160 cm^{-1} . These two peaks correspond to the two NH_2 rocking vibrations in the planar $\text{NH}_2\text{-CO-NH}_2$ urea molecule. The peak at 1468 cm^{-1} corresponds to the anti-symmetric NCN stretching mode and the peak at 1540 cm^{-1} to a NH_2 bending mode. The 1578 and 1647 cm^{-1} urea peaks are also visible and correspond to stretching modes of the free and hydrogen bonded C-O group. The potassium chlorate shows its fingerprint peak at 930 cm^{-1} very clearly.

Figure 3 shows the remote Raman spectra of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) with 10 seconds integration time, equivalent to 150 laser pulses.

Gypsum and epsom salt are both hydrated sulfates and therefore show similar Raman peaks corresponding to the symmetric stretching vibrations ν_1 in the sulfate ions SO_3 at 1008 and 984 cm^{-1} respectively. The slight difference in peak positions and the sharp contrast in the O-H stretching region ($\sim 3400\text{ cm}^{-1}$) are enough to differentiate between both compounds at 430 meters.

Figure 4 shows the remote Raman spectra of dry ice (solid CO_2) and water ice (solid H_2O) with 10 seconds acquisition time. Dry ice and water ice are commonplace in the Solar System. Both spectra are very distinct. Carbon dioxide spectrum shows its characteristic doublet at 1284 and 1392 cm^{-1} while water ice shows the sharper solid water peak at $\sim 3100\text{ cm}^{-1}$. This peak depends on temperature and can help in determining the temperature of the measured water ice.

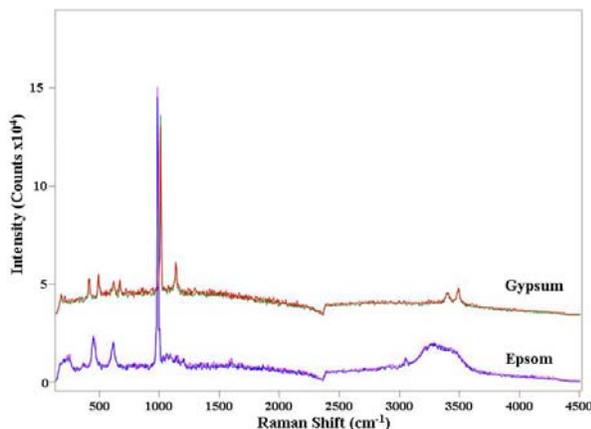


Figure 3: Remote Raman spectra of gypsum and MgSO_4 with 10 s acquisition time at 430 m range. Two

consecutive spectra are shown for each sample to demonstrate repeatability.

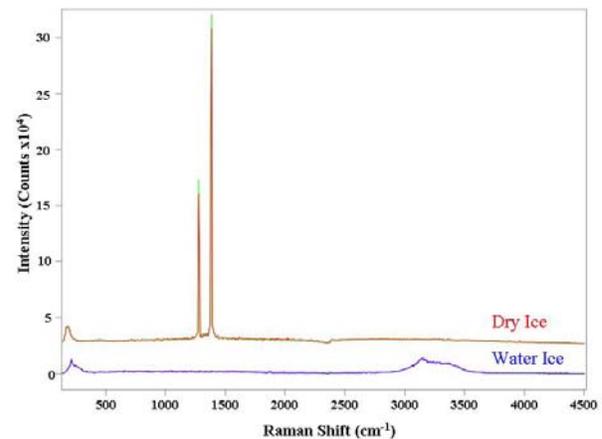


Figure 4: Remote Raman spectra of CO_2 ice and water ice with 10 s acquisition time at 430 meter range. Two consecutive spectra are shown for each sample to demonstrate repeatability.

References: [1] Misra A. K. et al. (2012) Applied Spec. 66, 1279–1285. [2] Wiens., et al. (2016) LPSC, this conf.