

A Raman spectroscopy comparison of an iron-bearing and a non-iron-bearing sulphate at both green and UV excitation wavelengths. D. Hamilton¹, M.G. Daly¹, E.A. Cloutis², K. Tait³, ¹Centre for Research in Earth and Space Science, York University, Toronto, ON, Canada, M3J 1P3 (dalym@yorku.ca), ²Department of Geography, University of Winnipeg, Winnipeg, MB, Canada, R3B 2E9, ³Royal Ontario Museum, Toronto, ON, Canada, M5S 2C6.

Introduction: Both NASA and ESA are sending Raman instruments with green excitation wavelengths on their next Mars rover missions. NASA is also sending a UV Raman instrument (SHERLOC) on the Mars 2020 rover. As Raman intensity is theoretically proportional to the fourth power of the excitation frequency, it is believed that UV excitation would be ideal for the detection of small concentrations of biosignatures. Though this assumption has proved true in the lab using a simple quartz matrix [1][2], the same may not necessarily be true when considering a matrix more representative of the surface of Mars.

Whether one performs UV Raman spectroscopy on individual iron-bearing Mars analogue minerals (e.g. jarosite, nontronite, montmorillonite, magnetite) or a complex mixture matrix, many common planetary surface minerals show nearly complete absorption over a wide range of UV wavelengths. The combination of strong UV absorption and this weak inelastic scattering phenomenon result in few minerals that can be identified by UV Raman spectroscopy. Changing the excitation wavelength within the UV region may not be of significant benefit due to the broadness of the UV absorption. Minerals that contain transition metals exhibit this deep UV absorption.

We compare the Raman signal obtained at both green (532nm) and UV (266nm) excitation wavelengths for both an iron bearing sulphate (natrojarosite), and a non-iron bearing sulphate (synthetic gypsum). The result is that the gypsum exhibits Raman peaks for both green and UV excitation, while the natrojarosite only exhibits Raman peaks for green excitation. The suggested mechanism is that ligand-metal charge transfers cause intense electronic transitions in the UV, while crystal field splitting breaks the degeneracy of iron 3d orbitals, broadening the peaks by providing more transition possibilities.

Sulphate minerals:

Natrojarosite $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ was selected for the iron bearing sulphate as the jarosite group is predicted to be the dominant iron sulphate on the surface of Mars. Natrojarosite forms in highly acidic aqueous solutions, downstream from sulphides and primary basaltic materials [3]. Jarosite (K cation instead of Na cation) has been found using Mossbauer spectroscopy [4] on the surface of Mars by the Opportunity MER rover, and within patches of iron smectites by the

CRISM instrument on the MRO orbiter [3]. Though major jarosite deposits are assumed to be very localized on the surface of Mars, it is suggested [5] that it is an integral component in the globally mobilized dust, thereby spreading small amounts of the mineral around the planet. This work used natrojarosite with grain size < 45 microns.

Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was selected for the non-iron bearing sulphate as it is suggested to be the dominant calcium sulphate on Mars [6]. It has been found in vast areas by the OMEGA instrument on the Mars Express orbiter [6]. It forms as an evaporite of saline lakes. To ensure no trace iron impurities were in the sample used, a batch of synthetic gypsum (< 45 microns) was selected for examination. This sample is highly hydroscopic, thus O-H stretching intensities could not be expected to be consistent from one trial to the next. This factor does not affect the overall goals of this study. Also differing amounts and locations of hydrogen bonding could cause slight shifts in the sulphate ion vibrational frequencies.

Method:

Green (532nm)- The instrument used for the green excitation was a Horiba LabRAM. This was provided by the Royal Ontario Museum (Toronto, Canada). Calibration was done using the single stretching peak of silicon.

Ultraviolet (266nm)- Our experimental set up for UV excitation was the same as that used in Eshelman et al.[2], except for two minor changes. Firstly, the diffraction grating was changed from a 2400 lines/mm to a 3600 lines/mm for additional resolution. As well, a dichroic mirror was added so that a 180 degree collection geometry could be used. Calibration was done using multiple peaks of the amino acid L-alanine.

Results:

Gypsum (532nm) - The most intense peak occurs at 1011 cm^{-1} and corresponds to the symmetric stretch of the sulphate ion. The less intense band at the higher wavenumber 1138 cm^{-1} corresponds to the antisymmetric stretch of that ion. Bands at 418 cm^{-1} and 622 cm^{-1} and 673 cm^{-1} correspond to bending modes. The first two, out-of-plane bends, and the last two, in-plane bending modes. These values correspond with published data [1] for natural gypsum samples. The differences are within the uncertainty of the measurements.

The water symmetric and asymmetric stretches were found at 3407 and 3495 cm^{-1} , respectively.

Gypsum (266nm) - As expected, the same number of peaks were detected. The sulphate stretching peaks were shifted to slightly higher frequencies at 1018 and 1146 cm^{-1} . The two out-of-plane bending remained while the in-plane bending modes were similar at 622 and 675 cm^{-1} . The water symmetric and asymmetric stretches were found at 3422 and 3507 cm^{-1} , respectively. These shifts are attributed to the hygroscopic nature of the sample. The final result is a superposition of both water types (adsorbed and structural).

Natrojarosite (532nm) - An intense peak occurs at 1009 cm^{-1} and corresponds to the symmetric stretch of the sulphate ion. The more intense band at the higher wavenumber of 1112 cm^{-1} corresponds to the antisymmetric stretch of that ion. A second antisymmetric stretch is located at 1152 cm^{-1} and is caused by a degeneracy of that stretch in the presence of the sodium cation. Published data (Liu and Wang) places the symmetric stretch at 1010 cm^{-1} and the two antisymmetric stretches at 1109 and 1151 cm^{-1} , in agreement with our data. A band at 622 cm^{-1} corresponds to an in plane bending mode and a band at 445 cm^{-1} corresponds to an out of plane bending mode of the sulphate ion. These agree well with published values [8] of 625 and 451 cm^{-1} , respectively. Bands observed at 227, 292, and 364 cm^{-1} correspond to O-Fe stretching modes that agree well with the data of Sasaki. There is one peak observed at 536 cm^{-1} . It is unclear if this is an O-H bending mode or another O-Fe mode as it falls in between published data.

Natrojarosite (266nm) - No discernible information is available from this spectra other than a weak sulphate stretch around 1022 cm^{-1} . The intensity is three orders of magnitude lower than that of gypsum and is on the same order as the noise.

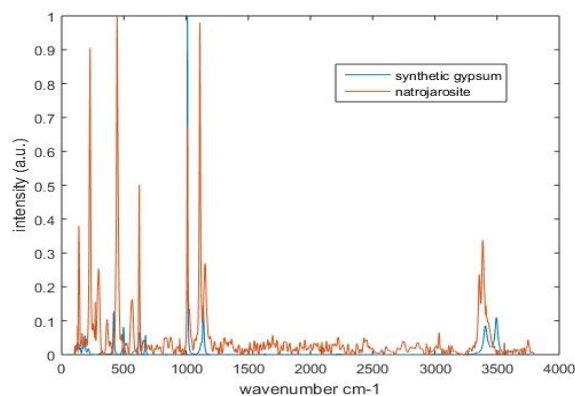


Figure 1. Raman spectra using green laser. Background removal using Crystal Sleuth software.

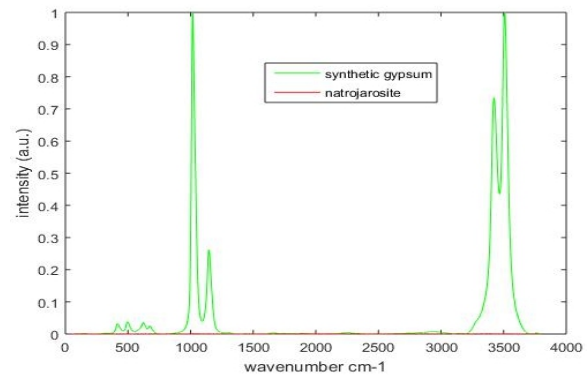


Figure 2. Raman spectra using UV laser. Background removal using Crystal Sleuth software.

Conclusion: Crystal field splitting in the Fe(III) atoms in octahedral coordination causes a splitting in the degeneracy of the 3d orbitals. The transition of an electron from an oxygen 2p orbital to an iron 3d orbital (ligand-metal charge transfer) falls within the UV range. These transitions are both Laporte allowed and spin allowed, thus, they are very intense. There are many further splittings in the 3d degeneracy due to spin orbit coupling, the Jahn-Teller effect [9], and asymmetric ligand site filling (the iron in natrojarosite is attached to four hydroxyls and two oxygens). The multiple decrease of degeneracy causes a broad absorption. The combination of the intensity of the transitions, their broadness, and the weakness of inelastic scattering produces poor spectra in the UV in iron-containing sulphate and natrojarosite. The non-iron-bearing sulphate, gypsum, produces usable spectra at both excitation wavelengths because it does not experience ligand-metal charge transfer. Cloutis et al [10] performed spectral reflectance measurements on a natrojarosite + goethite combination that exhibited a reflectance minima at 262 nm, which is attributed to oxygen-iron charge transfer, thereby supporting our results. The spectra found in the same study of many iron oxides show similar reflectance minima between 240 and 250 nm.

References:

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