

RAMAN SPECTROSCOPIC INVESTIGATION OF FERROUS SULFATE HYDRATES. S. K. Sharma¹, C. H. Chio² and D. W. Muenow², ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, Hawaii 96822, USA (sksharma@soest.hawaii.edu); ²Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822, USA.

Introduction: There is a growing interest in the study of sulfate minerals on the surface of Mars, supported by the discovery of jarosite at Meridiani Planum [1-3]. There is also the possibility of finding hydrous sulfate minerals in the permafrost, located at the polar regions. Sulfate minerals often precipitate in a variety of hydration states in the presence of liquid water. The spectra of suspected sulfate minerals obtained by reflectance spectroscopy have broad spectral features [4, 5], making the identification of mixtures of hydrous sulfates difficult. We therefore carry out an investigation of various forms of ferrous sulfate (FeSO_4) hydrates by Raman spectroscopy. Our objective is to unambiguously distinguish between the hepta-, tetra-, and monohydrates of FeSO_4 . We also employ isotope substitution and low temperature techniques to help understand the unique spectral features of these hydrates in relation to changing molecular structures. Low temperature studies are particularly important for planetary missions as the Raman spectra of hydrous minerals often differ substantially in comparison to those acquired at ambient temperature.

Experimental: Reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite) was used for the preparation of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite) and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (szomolnokite) by heating in air and recrystallization in dilute sulfuric acid, respectively. The 488-nm radiation from an Ar-ion laser was used for excitation. Raman spectra were collected using a Spex Triplemate spectrometer equipped with a CCD detector. The spectra of these hydrates were acquired at ambient conditions and at reduced temperatures (down to 8 K) in a helium cryostat. Deuterated analogs were prepared by recrystallization of the monohydrate in D_2O . Further details regarding to sample preparation and instrumentation can be found elsewhere [6].

Results and Discussion: The Raman spectra of the hepta-, tetra-, and monohydrates of FeSO_4 are shown in Fig. 1. The symmetric stretching vibrational (ν_1) mode of the sulfate (SO_4) ion gives the most intense and narrow Raman line. Its wavenumber increases (976 to 1018 cm^{-1}) with lowering water content, and therefore can be used as a fingerprint for identifying FeSO_4 of different hydration states (Fig. 2). Similar trend has been reported for the hydrates of MgSO_4 [7], and the increase in wavenumber is believed to be caused by weakening H-bonding. The anti-symmetric stretching

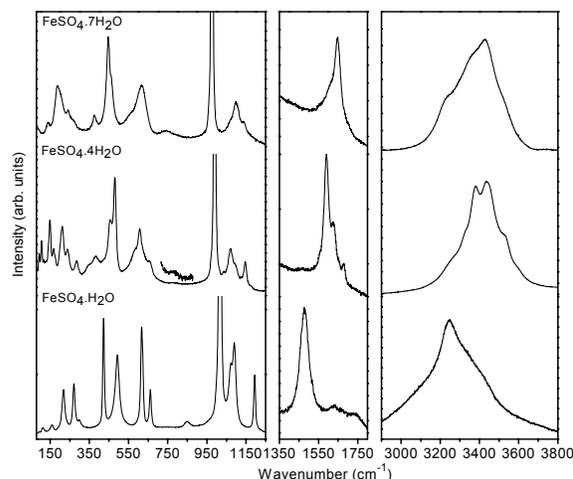


Fig. 1. Micro-Raman spectra of $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ ($n = 7, 4, 1$) at 298 K: lattice and SO_4 modes (left), H_2O bending modes (middle) and H_2O stretching modes (right).

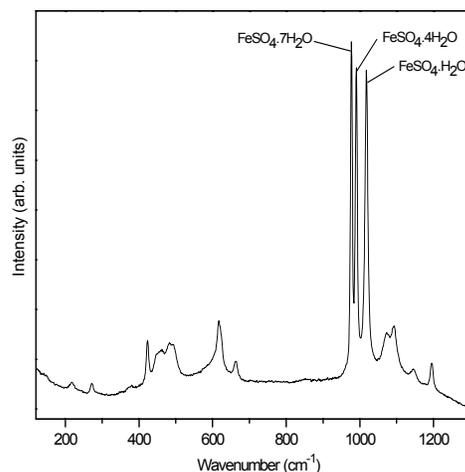


Fig. 2. Micro-Raman spectrum of a 1:1:1 (wt. ratio) mixture of FeSO_4 hydrates. The $\nu_1(\text{SO}_4)$ Raman lines from each of the hydrates are clearly visible.

vibrational mode of the SO_4 ion splits into three Raman lines (1050 to 1200 cm^{-1}), indicating the SO_4 tetrahedron ions in these hydrates are at sites of lower symmetry. The magnitude of crystal-field splitting strengthens with increasing geometric distortion of the SO_4 ion. Raman lines from the lattice vibrational modes differ considerably among these hydrates, reflecting large variations in the structural hierarchy with

changing hydration states [8].

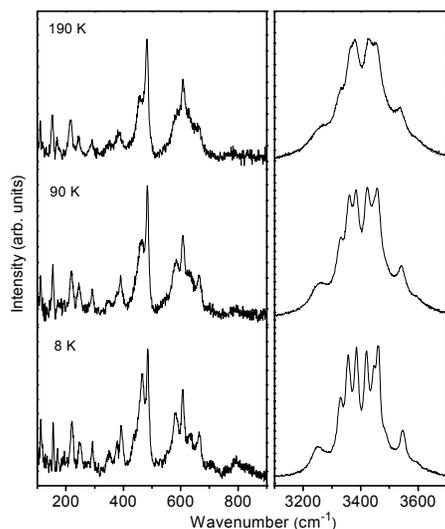


Fig. 3. Low temperature micro-Raman spectra of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$. Additional Raman lines are observed at low temperatures, indicating possible phase transitions.

The water molecules in hydrous minerals are often structurally non-equivalent. As a result, their vibrational modes give rise to complex, overlapping Raman bands. Four water vibrational bands can be resolved from the spectra of the hepta- and monohydrates, and six can be resolved from the tetrahydrate between 3200 and 3500 cm^{-1} . The water vibrational bands are influenced by a number of factors, including molecular

geometry, cation-water interactions, and H-bonding. Intermolecular coupling between structurally equivalent water molecules within the unit cell also yields additional Raman bands (factor group splitting). A broad shoulder at $\sim 3140 \text{ cm}^{-1}$ in the spectrum of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is believed to be an overtone band of the water bending mode, with its intensity enhanced by Fermi resonance. The water bands are substantially resolved at low temperatures. In the series of low-temperature spectra of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (Fig. 3), the occurrence of additional Raman bands in the lattice (350 to 400 cm^{-1}) and water stretching (3200 to 3600 cm^{-1}) regions likely indicates phase transition(s). No apparent transitions are visible in the low-temperature spectra of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, and the heptahydrate.

References: [1] Elwood Madden M. E. et al. (2004) *Nature*, 431, 821–823. [2] Klingelhoefer G. et al. (2004) *Science*, 306, 1740–1745. [3] Lane M. D. et al. (2004) *Geophys. Res. Lett.*, 31, L19702. [4] Pollack J. B. et al. (1990) *JGR*, 95, 14595–14627. [5] Blaney D. L. and McCord T. B. (1995) *JGR*, 100, 14433–14441. [6] C. H. Chio et al. (2005) *Spectrochim. Acta*, 61A, 2428–2433. [7] Wang A. et al. (2005) *GSA Annual Meeting*, Abstract #96030. [8] Hawthorne F. C. (1990) *Z. Kristallogr.*, 192, 1–52.

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Table 1. Observed Raman bands assignments of the hepta-, tetra-, and monohydrates of FeSO_4

$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Band Assignment [‡]
112	94, 106, 148, 168	138, 185	Lattice vibrations
158, 218, 271, 298	211, 240, 286, 346, 382	206, 241, 264, 376	$\nu_{\text{trans}}(\text{Fe}^{2+}, \text{H}_2\text{O})$
423, 492	456, 480	446, 465	$\nu_2(\text{SO}_4)$
615, 623, 661	607, 622, 659	565, 619	$\nu_4(\text{SO}_4)$
850	586, 784	747	$\nu_{\text{lib}}(\text{H}_2\text{O})$
1018	990	976	$\nu_1(\text{SO}_4)$
1073, 1092, 1194	1071, 1096, 1146, 1176(?)	1075, 1102, 1138	$\nu_3(\text{SO}_4)$
1478, 1630(?), 1735(?)	1590, 1629, 1679	1625, 1648	$\nu_2(\text{H}_2\text{O})$
3137	3272(?)	3227(?)	$2\nu_2(\text{H}_2\text{O})$
3246, 3333(?), 3410	3334, 3376, 3438, 3533, 3593	3371, 3436, 3506	$\nu_1(\text{H}_2\text{O}); \nu_3(\text{H}_2\text{O})$

[‡]Abbreviations: ν_1 , symmetric stretching; ν_2 , symmetric bending; ν_3 , anti-symmetric stretching; ν_4 , anti-symmetric bending; ν_{lib} , librational; ν_{trans} , translational