A thermal emission spectral library of rock-forming minerals

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Abstract. A library of thermal infrared spectra of silicate, carbonate, sulfate, phosphate, halide, and oxide minerals has been prepared for comparison to spectra obtained from planetary and Earth-orbiting spacecraft, airborne instruments, and laboratory measurements. The emphasis in developing this library has been to obtain pure samples of specific minerals. All samples were hand processed and analyzed for composition and purity. The majority are 710–1000 μm particle size fractions, chosen to minimize particle size effects. Spectral acquisition follows a method described previously, and emissivity is determined to within 2% in most cases. Each mineral spectrum is accompanied by descriptive information in database form including compositional information, sample quality, and a comments field to describe special circumstances and unique conditions. More than 150 samples were selected to include the common rock-forming minerals with an emphasis on igneous and sedimentary minerals. This library is available in digital form and will be expanded as new, well-characterized samples are acquired.

1. Introduction

The Thermal Emission Spectrometer (TES) instrument arrived at Mars on September 11, 1997, aboard the Mars Global Surveyor spacecraft. This instrument has obtained spectra of Martian surface materials [*Christensen et al.*, this issue (a), (b); *Smith et al.*, this issue] and is scheduled to map the entire surface of Mars over its 3 year mission [*Christensen et al.*, 1992]. This instrument will return over 10^9 high-resolution IR spectra of Martian surface materials. In addition, a broadband thermal-IR imager being developed for the 2001 Surveyor Orbiter will return over 10^{10} 100-m resolution, nine-point spectra covering the entire planet. A TES instrument will also be flown on the 2001 and 2003 Surveyor lander and rover missions that will return high spectral resolution data. In this paper, we present the laboratory measurements acquired in emission at Arizona State University that are designed to support the interpretation of the data returned from Mars. In addition, the library can be used to interpret data returned from the thermal infrared multispectral scanner (TIMS) [*Palluconi and Meeks*, 1985], the Advanced Spaceborne Thermal Emission and Reflectance Radiometer (ASTER) that is scheduled for launch on the Earth Observing Satellite (EOS) in 1999, and mineralogical and petrological laboratory studies. The purpose of this paper is to describe the method used to obtain a library of well-characterized, high-purity mineral samples and spectra that may be used for mineralogical determination.

Vibrational spectroscopy is based on the principle that vibrational motions occur within a crystal lattice at specific frequencies that are directly related to the crystal structure and elemental composition (i.e., mineralogy) [e.g., *Wilson et al.*, 1955; *Farmer*, 1974]. The fundamental frequencies of geologic materials typically correspond to wavenumbers less than 2000 cm^{-1} (greater than ~5 μm) and provide a diagnostic tool for identifying all minerals. An extensive suite of studies over the past 35 years has demonstrated the utility of vibrational spectroscopy for the quantitative determination of mineralogy and petrology [e.g., *Lyon*, 1962; *Lazerev*, 1972; *Farmer, 1974; Hunt and Salisbury*, 1976; *Salisbury et al.*, 1987, 1991; *Salisbury and Walter*, 1989; *Salisbury*, 1993; *Lane and Christensen*, 1997b; *Hamilton et al.*, 1997]. The fundamental vibrations within different anion groups such as CO_3, SO_4, PO_4, and SiO_4 produce unique, well-separated spectral bands that allow carbonates, sulfates, phosphates, silicates, oxides, and hydroxides to be readily identified. Additional stretching and bending modes involving major cations, such as Mg, Fe, Ca, and Na, allow further mineral identification, such as excellent discrimination of minerals within the silicate and carbonate groups.

A variety of techniques have been developed that measure emitted, reflected, transmitted, or scattered energy as a function of wavelength to detect absorption features due to the fundamental vibrational modes. The emission spectroscopy technique used here has been applied previously in the laboratory [e.g., *Lyon*, 1965; *Low and Coleman*, 1966; *Conel*, 1969; *Griffiths*, 1972; *Christensen and Harrison*, 1993; *Ruff et al.*, 1997] and acquires spectra in a similar manner to remotely sensed data. This similarity allows for direct, quantitative comparison of laboratory spectra to remote sensing data sets.

2. Method

Samples were prepared through a process of crushing, sieving, and washing. Crushing was done either by hand using a rock hammer or through a jaw crusher. Samples were then dry-sieved using a Ro-tap mechanical sieve shaker, and the 710-1000 μm size fraction was separated. This size fraction was used because volume scattering effects that are introduced

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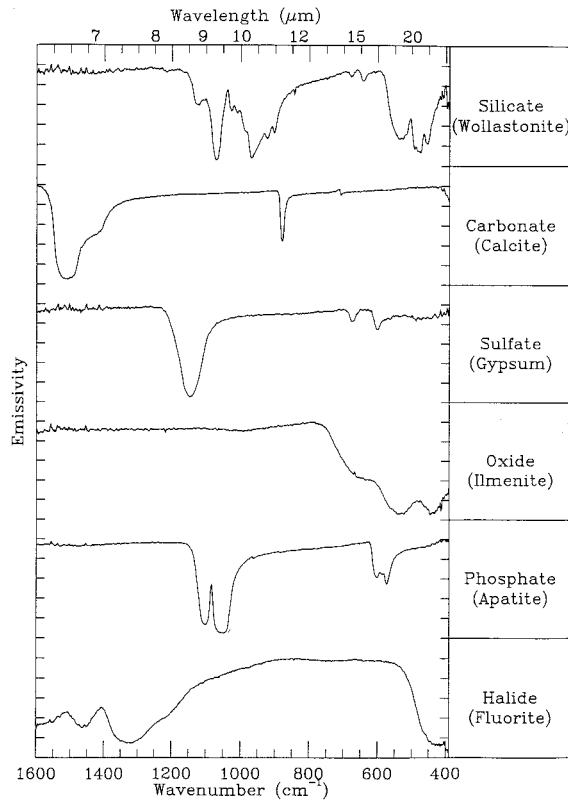
Figure 1. Example of library emission spectra (normalized) of several mineral classes demonstrating the wide variety in absorption band position and shape between each mineral class. Library sample numbers are (from top to bottom) ASU-60, 91, 82, 35, 96, 59.

with small particle sizes are minimized, it simulates the roughness of sandy and rocky surfaces, and grains are ideally randomly oriented to prevent preferential viewing of any crystal axis. For several samples, such as mica minerals, it was impractical to achieve a random orientation, and these are noted in the database. The samples were washed repeatedly using deionized water, acetone, or ethanol as appropriate to remove clinging fines, and the purest grains were selected by hand under a magnifying lens to ensure a high-quality sample. The purity and composition of each sample was determined by setting aside some of the final sample for electron microprobe and/or X-ray diffraction analysis. In cases where there was sufficient sample quantity, bulk analysis was also acquired. In the case of hand samples (which includes many of the carbonate, sulfate, and phosphate samples) and samples donated from the Hunt and Salisbury Collection at the U.S. Geological Survey (USGS), the standard sample preparation was not applied and grain size is not limited, but compositional information has been verified.

The particulate samples were poured into copper cups with a 3-cm internal diameter and 0.5-cm depth and were heated in an oven overnight at 80°C to increase the signal to noise ratio. The sample was not leveled to avoid inducing preferential crystal orientations. Lab spectra were acquired using a Mattson Cygnus 100 interferometric spectrometer equipped with a KBr beam splitter and an uncooled deuterated triglycine sulfate (DTGS) detector. The spectrometer has been adapted from transmission to emission capabilities by removing the

globar source and the mirror closest to it. The sample chamber is contained within a glove box external to the spectrometer, and both the spectrometer and the glove box were continuously purged with nitrogen gas during sample analysis to minimize atmospheric H_2O and CO_2, which also have absorption features in the $2000-400$ cm^{-1} region of the spectrum. Particulate samples were placed on a heater element to maintain an $\sim80°C$ temperature during spectral acquisition and raised into a water-cooled sample chamber that closely approximates a blackbody cavity. The temperature of the chamber is monitored, allowing for environmental energy reflected off the sample and into the spectrometer to be accounted for and calibrated out of the resultant spectrum. Energy emitted from a ~1-cm spot of the sample in a 37° cone is reflected off a paraboloid mirror and directed into the spectrometer through an emission port. A total of 270 scans at 2 cm^{-1} sampling are taken over a ~7 min period and averaged together by the spectrometer. In the case of a hand sample, active heating during measurement is not possible. Hand samples are taken directly from the oven and placed into the sample chamber, and 180 scans are taken over a period of ~5 min to minimize the effects of sample cooling.

3. Calibration

The calibration method is a variation of method 1 of *Christensen and Harrison* [1993], as described in detail by *Ruff et al.* [1997]. This one-temperature method requires only a single
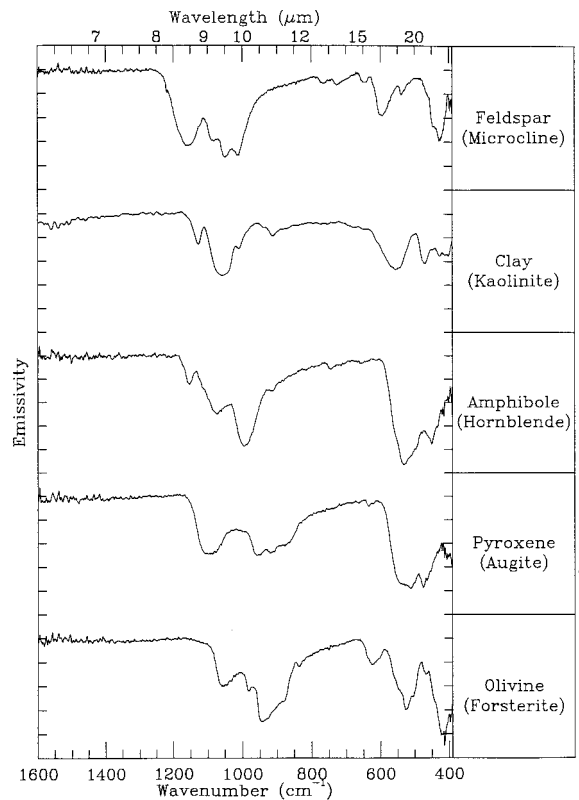

Figure 2. Major silicate subclass library emission spectra demonstrating differences in both band shape and position as a result of sample mineralogy. Ticks on the *y* axis are separated by 0.05 emissivity, and each spectrum has a maximum emissivity of 1. Library sample numbers are (from top to bottom) ASU-57, 178, 66, 54, 8.

measurement of each sample and defines all of the possible energy contributions to the spectrum in terms of radiance. Blackbody measurements at two temperatures are needed to derive detector temperature and an instrument response function. These blackbody measurements are made only once during a session of up to ~15 sample measurements. Sample temperature is determined spectrally at the wavelength of the highest brightness temperature. Reflected environmental energy is calculated and removed from the measured radiance with knowledge of the controlled environment energy and the use of Kirchhoff's law, which relates reflectivity and emissivity ($R = 1 - \varepsilon$) [*Salisbury et al.*, 1994]. The resulting sample radiance is divided by a calculated blackbody radiance curve at the temperature of the sample to obtain sample emissivity. This method assumes that the emissivity of the sample is unity at one point or more in the spectrum. Repeatability between sessions is better than 1% emissivity, and accuracy in most cases is within 2% emissivity [*Ruff et al*, 1997].

4. Data and Documentation

The library is available online in digital form, currently at http://tes.la.asu.edu. This paper serves as a reference document for the digital library, and users are requested to follow the guidelines posted on the Web site for referencing samples donated by external sources (e.g., National Museum of Natural History and Hunt and Salisbury). Attached to each spectrum are database fields that describe the sample. In some cases, the mineral has been renamed as a result of chemical analysis, but the original mineral name, source, and sample number have been retained in separate database fields. A sample quality field has been included to provide a quick assessment of sample purity. This field contains three degrees of sample purity: (1) the mineral and spectra are of high purity and quality; (2) there are minor impurities, but overall quality is still good; (3) the sample contains significant impurities which may significantly influence its spectrum. Also included with the database is a comment field that is used to describe special circumstances, unique conditions, and individual caveats. Other fields included are visual inspection results, donor history, bulk oxides, microprobe oxides, X-ray diffraction analysis results, and particle size.

Samples of the library spectra are shown in Figures 1–3. Mineral classes are easily distinguished on the basis of major absorptions present in different wavelength regions (Figure 1). Smaller compositional and structural variations also have a significant influence on band position and shape, as demonstrated with the silicate subclasses shown in Figure 2. Figure 3 shows the fine compositional and structural variation that causes distinct spectral differences within a mineralogical subtlass. The presence of distinct spectral features in a wide variety of minerals allows for laboratory and remote sensing mineralogical determinations using this data set.

Probably the best known and most commonly cited thermal infrared spectral library published to date is that of *Salisbury et al.* [1991]. This library was published in order to provide reflection rather than transmission measurements and to include spectral information to shorter wavelengths (2 μm) than was available in existing reflection/emission works. Reflectance spectra in the Salisbury et al. library were acquired via biconical reflectance measurements, and five samples have hemispherical reflectance spectra available as well. Although Kirchhoff's law ($R = 1 - \varepsilon$) [*Nicodemus*, 1965] is commonly used
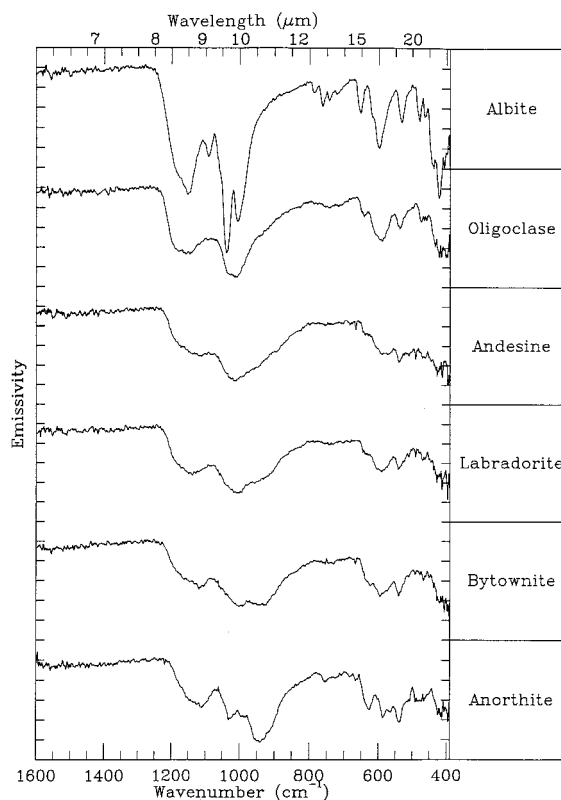

Figure 3. Library emissivity spectra of the plagioclase feldspar series. This figure demonstrates a high degree of discriminability between minerals within a single subclass. Ticks on the *y* axis are separated by 0.05 emissivity, and each spectrum has a maximum emissivity of 1. Library sample numbers are (from top to bottom) ASU-174, 22, 175, 176, 177, 178.

to predict spectral emissivity from reflectance measurements, *Salisbury et al.* [1991] demonstrated that this conversion is not applicable to biconical reflectance measurements in a quantitative sense. Instead, hemispherical reflectance spectra must be used if an accurate relationship to emission measurements is needed (Figure 4). The directional nature of the radiation measured by the biconical method does not adequately represent the infrared radiation scattered in all directions as do the emission and hemispherical reflectance measurements. Because both the Arizona State University and Salisbury et al. libraries contain samples acquired from the National Museum of Natural History, it was possible to compare a few samples common to both libraries (Figure 5). As in the case of the quartz shown in Figure 4, the biconical reflectance spectrum displays anomalous spectral features, especially at short wavelengths near the Christiansen frequency. This disparity is problematic if quantitative analysis of thermal emission measurements is desired, such as in the case of multimineralic (rock) spectra; in such cases, biconical spectra should be avoided, and hemispherical or emission spectra used instead.

5. Conclusion

The library currently consists of more than 150 mineral samples and is continually expanding. The library is not comprehensive, as collection and characterization of many of the library samples is driven by individual research interests, including several systematic mineralogical studies such as pyrox-
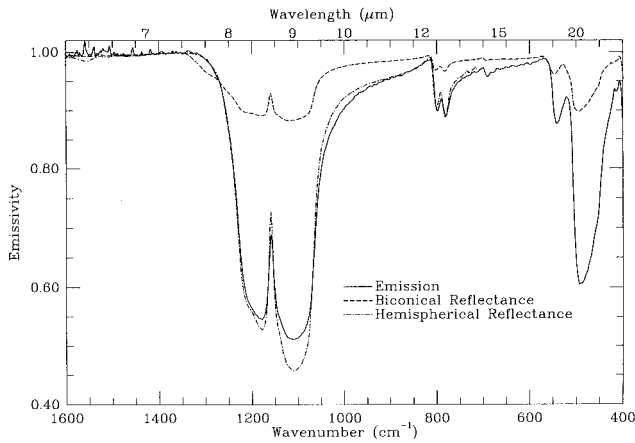
Figure 4. The spectral differences between three spectra of quartz, one acquired in emission, one in biconical reflectance [*Salisbury et al.*, 1991], and one in hemispherical reflectance [*Salisbury et al.*, 1991]. Both reflectance measurements are plotted as emissivity using Kirchhoff's law. The ASU quartz sample is not of the same physical sample as the Salisbury et al. quartz but is assumed to be comparable due to the simplicity of the mineral chemistry. The biconical reflectance spectrum displays anomalous spectral features in the shortest wavelength reststrahlen bands in the 1000–1300 cm^{-1} region.

ene, feldspar, clay, and evaporate mineral series [*Lane and Christensen*, 1997a; *Lane*, 1997; *Piatek*, 1997; *Hamilton*, 1998; *Ruff*, 1998]. However, with its emphasis on rock-forming minerals, the library contains a wide variety of minerals that will be useful in application to many geological problems. The major emphasis of this library is the careful and thorough sample documentation, sample preparation, and acquisition of emission spectra for both qualitative and quantitative spectroscopic research and comparison to remotely sensed data.
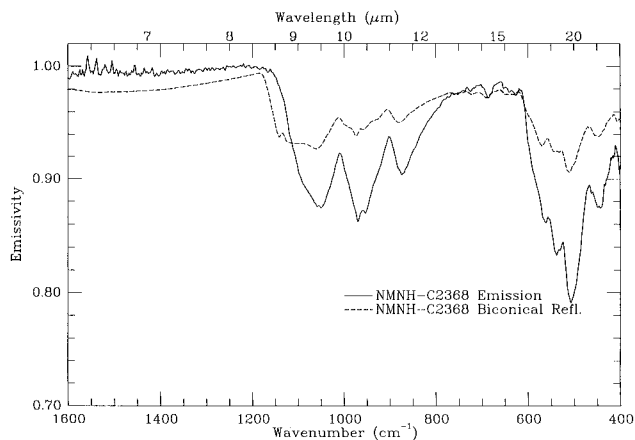

Figure 5. Emission and biconical reflectance spectra of orthopyroxene NMNH-C2368. The physical samples are different, but comparison of both samples' chemical analyses verifies that the compositions are virtually identical. As with the quartz shown in Figure 4, anomalous spectral features are present in the biconical reflectance spectrum in the shortest wavelength reststrahlen bands.

References

Christensen, P. R., and S. T. Harrison, Thermal infrared emission spectroscopy of natural surfaces: Application to desert varnish coatings on rocks, *J. Geophys. Res.*, *98*, 19,819–19,834, 1993.
Christensen, P. R., et al., Thermal Emission Spectrometer Experiment: Mars Observer mission, *J. Geophys. Res.*, *97*, 7719–7734, 1992.
Christensen, P. R., J. L. Bandfield, M. D. Smith, V. E. Hamilton, and R. N. Clark, Identification of a basaltic component on the Martian surface from Thermal Emission Spectrometer data, *J. Geophys. Res.*, this issue (a).
Christensen, P. R., et al., Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: Evidence for near-surface water, *J. Geophys. Res.*, this issue (b).
Conel, J. E., Infrared emissivities of silicates: Experimental results and a cloudy atmosphere model of spectral emission from condensed particulate mediums, *J. Geophys. Res.*, *74*, 1614–1634, 1969.
Farmer, V. C., *The Infrared Spectra of Minerals*, 539 pp., Mineral. Soc., London, 1974.
Griffiths, P. R., Infrared emission spectroscopy, I, Basic considerations, *Appl. Spectrosc.*, *26*, 73–76, 1972.
Hamilton, V. E., Thermal infrared emission spectroscopy of the pyroxene mineral series and pyroxene-bearing lithologies, Ph.D. dissertation, Ariz. State Univ., Tempe, 1998.
Hamilton, V. E., P. R. Christensen, and H. Y. McSween Jr., Determination of Martian meteorite lithologies and mineralogies using vibrational spectroscopy, *J. Geophys. Res.*, *102*, 25,593–25,603, 1997.
Hunt, G. R., and J. W. Salisbury, Mid-infrared spectral behavior of metamorphic rocks, *Environ. Res. Pap. 543-AFCRL-TR-76-0003*, 67 pp., Air Force Cambridge Res. Lab., Hanscom AFB, Mass., 1976.
Lane, M. D., Thermal emission spectroscopy of carbonates and evaporites: Experimental, theoretical, and field studies, Ph.D. dissertation, Ariz. State Univ., Tempe, 1997.
Lane, M. D., and P. R. Christensen, Thermal emission spectroscopy of aqueously precipitated minerals similar to those in the SNCS, Early Mars: Geologic and Hydrologic Evolution, Physical and Chemical Environments and the Implications for Life, *LPI Contrib.*, *916*, 49–50, 1997a.
Lane, M. D., and P. R. Christensen, Thermal infrared emission spectroscopy of anhydrous carbonates, *J. Geophys. Res.*, *102*, 25,581–25,592, 1997b.
Lazerev, A. N., *Vibrational Spectra and Structure of Silicates*, 302 pp., Consult. Bur., New York, 1972.
Low, M. J. D., and I. Coleman, The measurement of infrared emission spectra using multiple-scan interferometry, *Spectrochim. Acta*, *22*, 369–376, 1966.
Lyon, R. J. P., Evaluation of infrared spectroscopy for compositional analysis of lunar and planetary soils, final rep. contract NASr 49(04), Stanford Res. Inst., Stanford, Calif., 1962.
Lyon, R. J. P., Analysis of rocks by spectral infrared emission (8–25 microns), *Econ. Geol.*, *60*, 715–736, 1965.
Nicodemus, F. E., Directional reflectance and emissivity of an opaque surface, *Appl. Opt.*, *4*, 767–773, 1965.
Palluconi, F. D., and G. R. Meeks, Thermal infrared multispectral scanner (TIMS): An investigator's guide to TIMS data, Jet Propul. Lab., Pasadena, Calif., 1985.
Piatek, J. L., Vibrational spectroscopy of clay minerals: Implications for remote sensing of terrestrial planetoids, Master's thesis, Ariz. State Univ., Tempe, 1997.
Ruff, S. W., Quantitative thermal infrared emission spectroscopy applied to granitoid petrology, Ph.D. dissertation, Ariz. State Univ., Tempe, 1998.
Ruff, S. W., P. R. Christensen, P. W. Barbera, and D. L. Anderson, Quantitative thermal emission spectroscopy of minerals: A technique for measurement and calibration, *J. Geophys. Res.*, *102*, 14,899–14,913, 1997.
Salisbury, J. W., Mid-infrared spectroscopy: Laboratory data, in *Re-*

mote Geochemical Analysis: Elemental and Mineralogical Composition, edited by C. Pieters and P. Englert, 594 pp., Cambridge Univ. Press, New York, 1993.

Salisbury, J. W., and L. S. Walter, Thermal infrared (2.5–13.5 μm) spectroscopic remote sensing of igneous rock types on particulate planetary surfaces, *J. Geophys. Res*., *94*, 9192–9202, 1989.

Salisbury, J. W., L. S. Walter, and N. Vergo, Mid-infrared (2.1–25 μm) spectra of minerals: First edition, *U.S. Geol. Surv. Open File Rep*., *87–263*, 1987.

Salisbury, J. W., L. S. Walter, N. Vergo, and D. M. D'Aria, *Infrared (2.1–2.5 μm) Spectra of Minerals*, 267 pp., Johns Hopkins Univ. Press, Baltimore, Md., 1991.

Salisbury, J. W., A. Wald, and D. M. D'Aria, Thermal infrared remote sensing and Kirchhoff's law, 1, Laboratory measurements, *J. Geophys. Res*., *99*, 11,897–11,911, 1994.

Smith, M. D., J. L. Bandfield, and P. R. Christensen, Separation of atmospheric and surface spectral features in Mars Global Surveyor Thermal Emission Spectrometer (TES) spectra, *J. Geophys. Res*., this issue.

Wilson, E. B., Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*, McGraw-Hill, New York, 1955.

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