

THE MILLIMETER-WAVELENGTH SULFUR DIOXIDE ABSORPTION SPECTRA MEASURED UNDER SIMULATED VENUS CONDITIONS

A Masters Thesis Proposal

Presented to

The Academic Faculty

by

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Abstract

The objective of the proposed research is to develop a mathematical model that accurately estimates the opacity of sulfur dioxide in a carbon dioxide atmosphere under conditions characteristic of the Venus troposphere based on extensive laboratory measurements. High precision measurements of the millimeter-wavelength properties of sulfur dioxide are being conducted under multiple pressure and temperatures. These measurements are being conducted in both W-band and F-band (2-3 and 3-4 millimeter-wavelengths). The results of this research will significantly improve the understanding of the millimeter-wavelength emission spectrum of Venus and possibly determine the source of variations in the Venus millimeter-wavelength emissions.

1 Introduction

Active and passive microwave remote sensing techniques have been extensively used in the study of our sister planet, Venus. Unlike Earth's atmosphere, the Venus atmosphere is mostly comprised of gaseous carbon dioxide (CO_2). CO_2 comprises 96.5% of the atmosphere along with gaseous nitrogen (N_2) at about 3.5%. The Venus atmosphere has multiple trace constituents such as sulfur dioxide (SO_2), carbon monoxide (CO), water vapor (H_2O), carbonyl sulfide (OCS), and sulfuric acid vapor (H_2SO_4) [10].

Two sulfur-bearing compounds dominate the millimeter-wave emission from Venus: sulfur dioxide (SO_2) and gaseous sulfuric acid (H_2SO_4). At higher pressures H_2SO_4 thermally dissociates, forming H_2O and SO_2 , both of which exhibit relatively small amounts of microwave absorption at the abundance levels present in the Venus atmosphere. Thus, in the deep atmosphere, only SO_2 and CO_2 have the potential to affect the observed microwave emission.

Utilizing the millimeter-wavelength system at the Planetary Atmospheres Laboratory at Georgia Institute of Technology it is possible to simulate the upper troposphere of Venus and take precision measurements of the millimeter-wavelength properties of sulfur dioxide. Using the measurements, a model can be created that accurately predicts the opacity of sulfur dioxide in the Venus atmosphere. This model will make it possible to determine the source of variations in the Venus millimeter-wavelength emission, such as were observed by Sagawa [7].

2 Laboratory Measurements of Sulfur Dioxide

Verifying millimeter-wavelength absorption spectrum of SO_2 is important for the study of the atmosphere of Venus. Making measurements under simulated Venus conditions

assures the accuracy of any model derived from such measurements. Described below is the theory, laboratory equipment, measurement procedure and derived uncertainties in the measurements of the millimeter-wavelength absorptivity of gaseous sulfur dioxide under simulated Venus conditions.

2.1 Measurement Theory

In this experimental program, quality factor (Q) of a resonant mode of a resonator is used to measure the absorption of a gas or gas mixture [5]. The quality factor of a resonance is given by [6]

$$Q = \frac{2\pi f_0 \times \text{Energy Stored}}{\text{Average Power Loss}} \quad (1)$$

where f_0 is the resonant frequency. The Q of a resonance can be measured directly from f_0 by dividing it by its half-power bandwidth (HPBW).

$$Q = \frac{f_0}{HPBW} \quad (2)$$

The Q of a lossy gas (ϵ'/ϵ'') and its opacity are related by

$$\alpha \approx \frac{\epsilon''\pi}{\epsilon'\lambda} = \frac{1}{Q_{gas}} \frac{\pi}{\lambda} \quad (3)$$

where ϵ' and ϵ'' are the real and imaginary permittivity of the gas, λ is the wavelength in km, and α is the absorptivity of the gas in Nepers/km (1 Neper = 8.686 dB). Since Q can be affected by more than just the gas added, the Q of the gas-filled resonator is given by

$$\frac{1}{Q_{loaded}^m} = \frac{1}{Q_{gas}} + \frac{1}{Q_r} + \frac{1}{Q_{ext1}} + \frac{1}{Q_{ext2}} \quad (4)$$

where Q_{loaded}^m is the measured quality factor of a resonance in the presence of a test gas, Q_{gas} is the quality factor of the gas under test, Q_r is the quality factor of the resonator in the absense of coupling losses, and Q_{ext1} and Q_{ext2} are the external coupling losses. Since the resonator used is symmetric, it is safe to assume $Q_{ext1} = Q_{ext2}$. Coupling losses can be derived from the transmissivity $t = 10^{-S/10}$, where S is the measured insertion loss of the resonator in decibels (dB) at the frequency of a particular resonance using the following relationship

$$t = \left[w \frac{Q^m}{Q_{ext}} \right]^2, \quad (5)$$

$$Q_{ext} = \frac{2Q^m}{\sqrt{t}} \quad (6)$$

Q_r is related to the measured Q at a vacuum by

$$\frac{1}{Q_{vac}^m} = \frac{1}{Q_r} + \frac{1}{Q_{ext1}} + \frac{1}{Q_{ext2}} \quad (7)$$

where Q_{vac}^m is the measured Q at a vacuum. Substituting equation 6 into equations 4 and 7 gives

$$\frac{1}{Q_{gas}} = \frac{1 - \sqrt{t_{loaded}}}{Q_{loaded}^m} - \frac{1 - \sqrt{t_{vac}}}{Q_{vac}^m} \quad (8)$$

where t_{loaded} and t_{vac} are the transmissivity of the resonance taken in loaded and vacuum conditions respectively. When gas is added to the resonator there is a shift in the center frequency corresponding to the refractive index of the test gas. Since the quality factor is reliant on the center frequency this will affect the comparison between the two measurements. This effect is called dielectric loading [1]. Dielectric matching can be achieved

by performing additional measurements of the quality factor with a lossless gas present. Adding the lossless gas shifts the center frequency of the resonances, and by adding more or less gas the center frequency can be adjusted to be exactly the same as the lossy gas. These measurements are used in place of the vacuum measurements in equation 8 and by converting Nepers/km to dB/km we can rewrite equation 3 as

$$\alpha = 8.686 \frac{\pi}{\lambda} \left(\frac{1 - \sqrt{t_{loaded}}}{Q_{loaded}^m} - \frac{1 - \sqrt{t_{matched}}}{Q_{matched}^m} \right) dB/km \quad (9)$$

2.2 Millimeter-Wavelength Measurement System

The high-sensitivity millimeter-wavelength system used for measuring the opacity of gaseous sulfur dioxide under Venus conditions is similar to the one used by Devaraj and Steffes [3] [2]. The system is comprised of two subsystems for measuring different bands of the millimeter-wavelength spectrum (W-band/F-band). The simulator consists of a glass pressure chamber capable of withstanding up to 3 bars of pressure along with a temperature chamber capable of operating up to 400K. The W-band subsystem is used for measurements in the 3-4 millimeter-wavelength range while the F-band system is used for the 2-3 millimeter-wavelength range. The following sections describe each subsystem and their components.

2.2.1 W-band Subsystem

The W-band measurement system is used to measure the 3-4 mm-wavelength properties of sulfur dioxide is shown in figure 1.

A synthesized swept signal generator (HP 83650B) is used to generate a signal in the 12.5-18.3 GHz range which is fed through a times-six active multiplier chain (AMC) via low-loss, high frequency coaxial cables. The radio frequency (RF) signal from the output port

of the Fabry-Perot resonator (FPR) is fed to a QuinStar Technology QMH series harmonic mixer. The local oscillator (LO) and the intermediate frequency (IF) are connected via an external diplexer. The harmonic mixer is locked to the 18th harmonic of the spectrum analyzer LO and is used in the “external mixer” mode with the spectrum analyzer (HP 8564E).

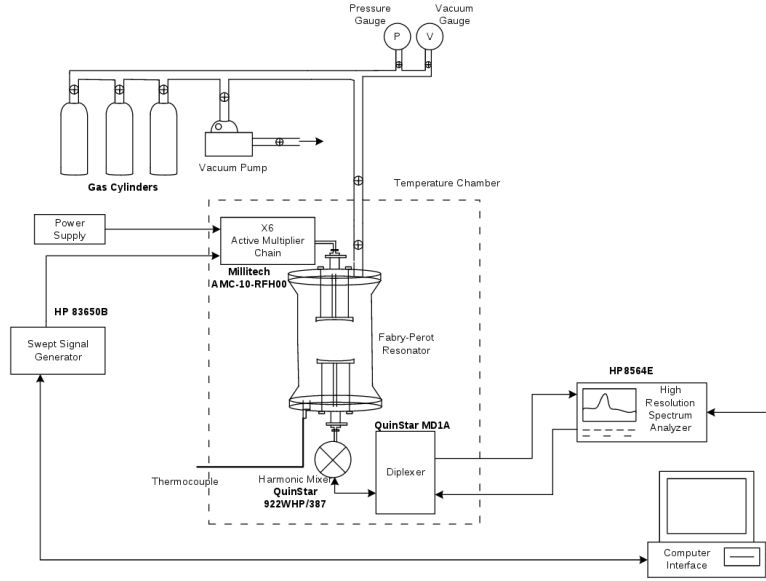


Figure 1: Block diagram of the W band measurement system. Solid lines represent the electrical connections and the arrows show the direction of the signal propagation. Valves controlling the flow of gasses are shown by small crossed circles.

2.2.2 F-band Subsystem

The F-band measurement system is used to measure the 2-3 mm-wavelength properties of sulfur dioxide and is shown in figure 2.

The swept signal generator (HP 83650B) is used to generate a signal in the 33-50 GHz range which is amplified and fed through a frequency tripler. The output of the tripler is fed to the input end of the FPR. The RF signal from the output port of the FPR is fed to

a harmonic mixer which can operate with an LO frequency as high as 18 GHz. An external diplexer is used to combine the IF and LO signals. For a particular RF and IF frequency, the LO frequency can be computed using

$$f_{LO} = \frac{f_{RF} - f_{IF}}{N_H} \quad (10)$$

where N_H is the lowest integer such that $f_{lo} < 18GHz$.

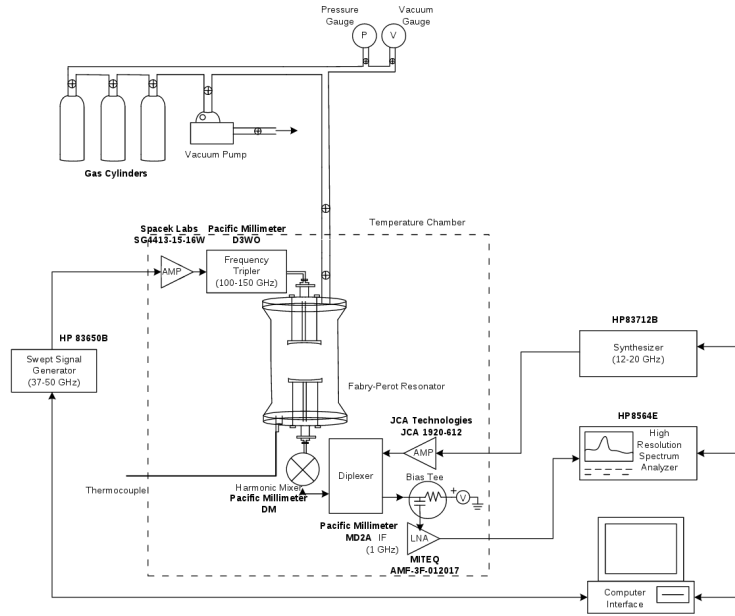


Figure 2: Block diagram of the F band measurement system. Solid lines represent the electrical connections and the arrows show the direction of the signal propagation. Valves controlling the flow of gasses are shown by small crossed circles.

2.3 Data Handling Subsystem

The data acquisition system consists of a computer connected to the spectrum analyzer (HP 8564E), swept signal generator (HP 83650B), and continuous wave (CW) signal generator (HP 83712B, the local oscillator for the F-Band system) via a general purpose

interface bus (GPIB). The instruments are controlled via Matlab script and their appropriate programming language. The software used is similar to Devaraj and Steffes [3] [2] with modifications for equipment changes.

2.4 Measurement Procedure

The most important prerequisite for performing measurement of gas properties is ensuring a leak-proof system. This is done through two methods, the first is by drawing a vacuum inside the FPR and verifying the integrity of the vacuum over time. The second way is by adding a positive pressure of CO_2 to the system and making sure there are no leaks in any of the connectors and valves. Ensuring a leak-proof system allows for not only precise measurements but also ensures no toxic gases are released into the testing environment.

After the system is ensured to be leak-proof and at a stable temperature, a vacuum is drawn and a measurement is taken using the appropriate subsystem (W-band for 3-4 mm-wavelengths, F-band for 2-3 mm-wavelengths). This allows for a base line measurement of the FPR's resonances and the Quality factor. Once this baseline is established the gas under test is added to the system.

Once the gas temperature has stabilized, another set of tests measuring the resonant frequencies along with the quality factors is taken. More gas is added and the procedure is repeated until all suitable pressures are taken. A vacuum is drawn once again but this time it is pumped overnight due to the gas being tested (SO_2) and its properties of "sticking" (or adsorbing) to metal. Another vacuum measurement is taken to measure any possible system error.

Once the second vacuum measurements are taken CO_2 is then added to the chamber until the resonances are matched to the same frequency of our test gas. Again measurements are taken and this is repeated for every pressure of the test gas. Once this is finished

a vacuum is again drawn and another test is taken.

Lastly the system is set up for a transmissivity test where we measure t (equation 5) for each given resonant frequency. The system is then set back up and is ready for a new test. Reference table 1 for the testing matrix being used.

3 Preliminary Results

Currently the millimeter-wavelength system is completely operational in the Planetary Atmospheres Laboratory at The Georgia Institute of Technology. Using this system, high precision measurements of SO_2 's millimeter-wavelength absorption have recently been completed as part of this work. A preliminary model of SO_2 's absorption properties is available from Suleiman's previous work on microwave laboratory measurements [10]. Additionally measurements of SO_2 's centimeter-wavelength absorption have recently been taken under deep Venus conditions [8] [9].

3.1 Millimeter-Wavelength Results

Only one previous measurement of SO_2 's mm-wavelength opacity under Venus simulated conditions has been done (see Fahd et. al. 1991) [4] This measurement was done using only one frequency (94.1 GHz) in the mm-wavelength spectra.

In our experiment, eight different frequencies have been already tested using the millimeter-wavelength system measuring 100 mbar of SO_2 along with separate tests at 1 bar CO_2 combined with the SO_2 and 2 bar of CO_2 combined with the SO_2 . This allows for a comparison with Fahd's model and with Suleiman's model at higher frequencies.

3.1.1 Absorption Model

The goal of the laboratory measurements is to create a mathematical model that accurately estimates the opacity of sulfur dioxide in a carbon dioxide atmosphere under all possible conditions of temperature, pressure, concentration, and frequency (fTPC space). For the data fitting process we will use data taken with the FPR along with data from the Planetary Atmospheres Laboratory centimeter-wavelength system [8] [9] to create a model that best fits the fTPC space.

Extrapolating models for SO_2 's absorption into the mm-wavelength allows for a good starting point in the model creation process. As visible in the following figures, the absorption model matches the same shape as previous models but is lower by about 20%. Finding a unified model for SO_2 's absorption will compensate for this change.

Figures 3, 4, and 5 show the initial data taken for SO_2 opacity in the 3-4 mm-wavelength range. It is clear that previous absorption models work well in predicting the shape of the millimeter-wavelength absorption spectrum of SO_2 .

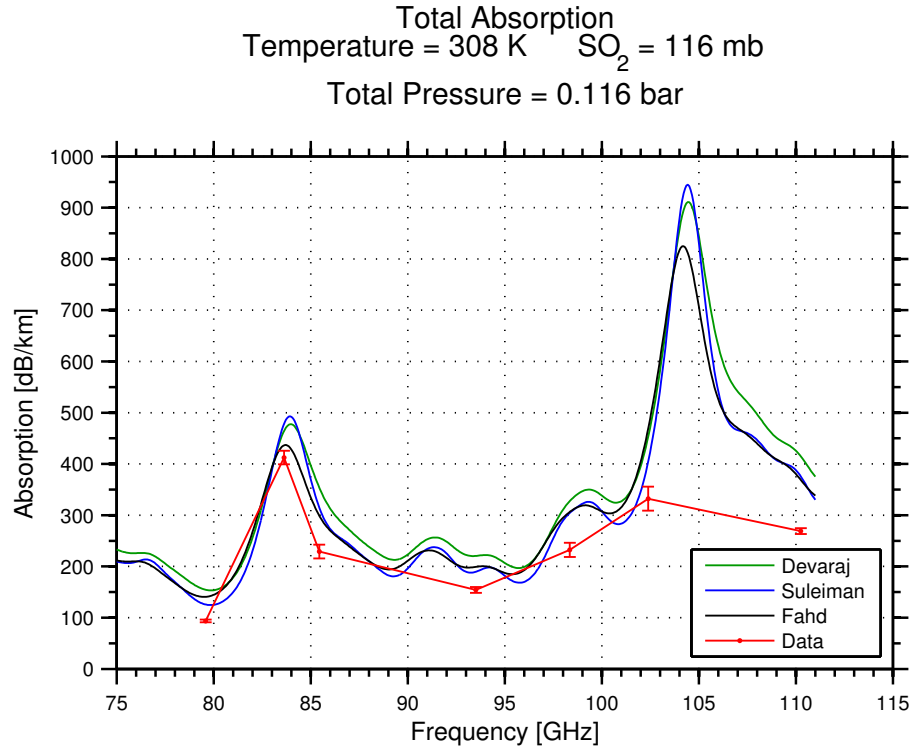


Figure 3: Measured absorption spectrum given 116 mbar of SO_2 at 308K in the W-band range. Shown for comparison are models from Devaraj (2011), Suleiman et al (1996), and Fahd and Steffes (1992).

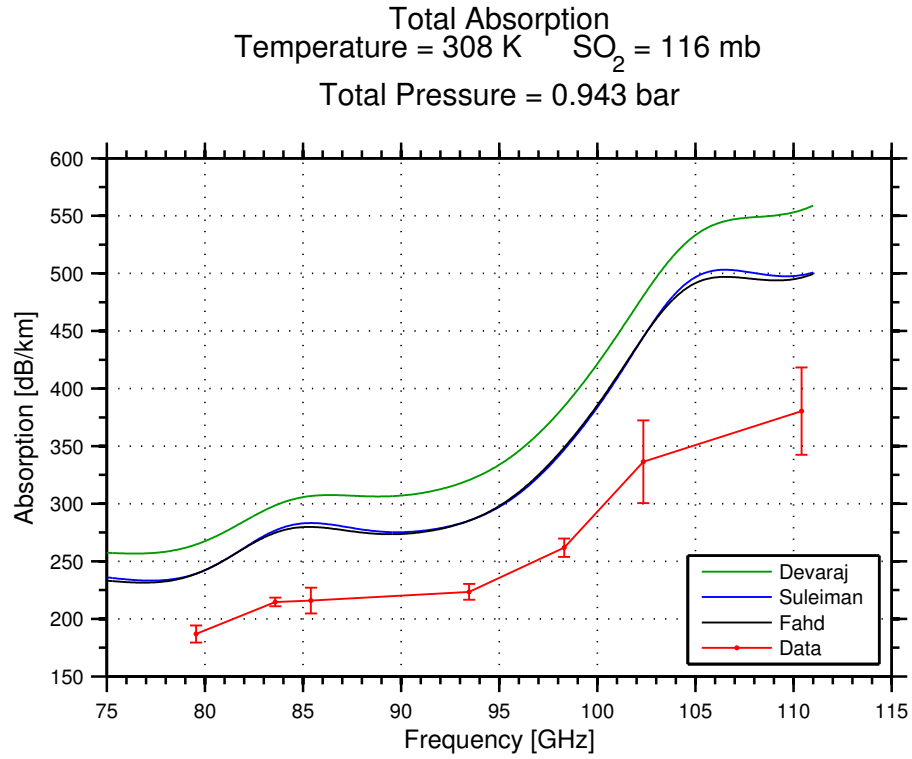


Figure 4: Measured absorption spectrum given 116 mbar of SO_2 and 827 mbar of CO_2 at 308K in the W-band range. Shown for comparison are models from Devaraj (2011), Suleiman et al (1996), and Fahd and Steffes (1992).

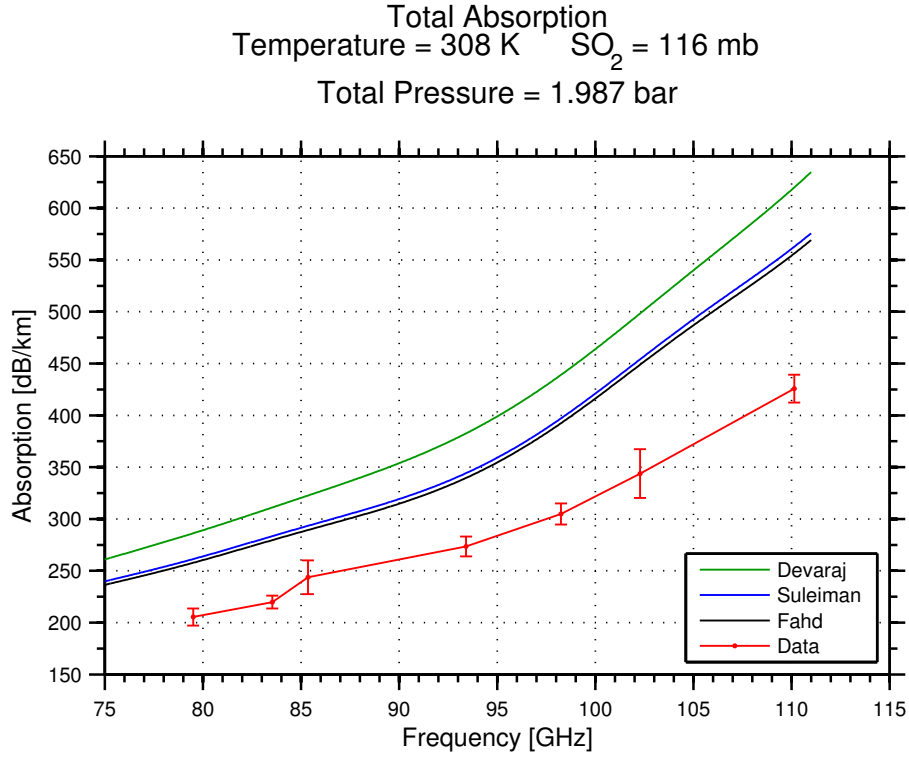


Figure 5: Measured absorption spectrum given 116 mbar of SO_2 and 1871 mbar of CO_2 at 308K in the W-band range. Shown for comparison are models from Devaraj (2011), Suleiman et al (1996), and Fahd and Steffes (1992).

4 Proposed Research

The objective of the proposed research is to advance the knowledge of the millimeter-wavelength properties of gaseous sulfur dioxide under Venus conditions. As part of the proposed research, extensive laboratory measurements of the W-band and F-band properties of sulfur dioxide under simulated upper Venus atmosphere are ongoing.

Upon completion of the laboratory measurements, efforts toward developing a unified model to estimate the centimeter and millimeter-wavelength opacity spectra of sulfur dioxide at various pressures, temperatures, and mixing ratios will be developed.

4.1 Significance of this Work

The primary objective of this millimeter-wavelength research is to better understand properties of gaseous sulfur dioxide under Venus conditions. The laboratory measurements will help create a model that accurately estimates the opacity of sulfur dioxide in a carbon dioxide atmosphere at any temperature or pressure. The new model will provide a unified opacity model for sulfur dioxide at the centimeter and millimeter-wavelengths. This model can be used for accurate retrievals of sulfur dioxide from ground-based and spacecraft-based radio observations.

4.2 Planned Work

Two major activities support this thesis: (1) laboratory measurements of 2-4 millimeter-wavelength properties of sulfur dioxide in a carbon dioxide atmosphere at two temperatures, 308 K and 348 K with pressures up to two bars and (2) the development of a model that best estimates sulfur dioxide's millimeter-wavelength absorption properties in Venus's upper troposphere. Both will be completed by Fall Semester 2014.

4.2.1 Laboratory Measurements

The ongoing millimeter-wavelength measurements focus on characterizing the opacity of sulfur dioxide in a carbon dioxide atmosphere temperatures of 308 K and 348 K. These will be the first precision measurements done of sulfur dioxide's absorption properties at millimeter-wavelengths. Previous work by Fahd [4] included a measurement done at 94.1 GHz but it did not utilize the high precision measurement tools available for this thesis.

The testing protocol involve laboratory measurements of the opacity of only sulfur dioxide as well as a mixture of sulfur dioxide and carbon dioxide at pressures of 1 bar and 2 bar. Table 1 shows a testing matrix of the tests to be done. Varying the sulfur

dioxide abundance as well as the temperature allows for an accurate model to be created and extrapolated to other pressure and temperature combinations.

Test Number	Gas under test	Pressure	Temperature	Subsystem
1	SO ₂	100 mbar	308 K	W-band
2	SO ₂	100 mbar	343 K	W-band
3	SO ₂	60 mbar	343 K	W-band
4	SO ₂	100 mbar	343 K	F-band
5	SO ₂	30 mbar	343 K	F-band
6	SO ₂	30 mbar	308 K	F-band

Table 1: Testing matrix for SO₂'s microwave absorption properties at 2-4 millimeter-wavelength.

4.2.2 Model Development

Completed and planned centimeter- [8] [9] and millimeter-wavelength measurements of the opacity of sulfur dioxide under Venus atmospheric conditions will be used to create a new model that accurately characterizes the centimeter- and millimeter-wavelength properties of sulfur dioxide. After the completion of the millimeter-wavelength laboratory measurements, both centimeter- and millimeter-wavelength data will be put into an optimization algorithm to create the best model estimate of the absorptivity of sulfur dioxide under Venus conditions.

4.3 Facilities Required

All of the facilities required for this work currently exist in the Planetary Atmospheres Laboratory at The Georgia Institute of Technology. The facilities include millimeter-wavelength test equipment, a Fabry-Perot resonator, a temperature chamber, pressure

and temperature gauges, and a computer running Matlab. Additional resources that are required and available are gas cylinders of carbon dioxide and sulfur dioxide. Computing resources necessary for model development are available at the Planetary Atmospheres Laboratory.

4.4 Milestone

Completed Work

- Completed setup of millimeter-wavelength system: January 2014
- Completed 3-4 millimeter-wavelength opacity of SO₂ under simulated Venus conditions: February 2014
- Completed 2-3 millimeter-wavelength opacity of SO₂ under simulated Venus conditions: April 2014
- Diagnosed issue with SO₂ pressure regulator and modified data accordingly: April 2014
- Submit thesis proposal: April 2014

Remaining Work

- Verify constituent inventory in SO₂ bottle and modify data accordingly: April 2014
- Develop consistent model for opacity of SO₂ incorporating the millimeter-wavelength measurements developed as part of this work and the centimeter-wavelength measurements made previously: June 2014
- Submit journal paper detailing the millimeter-wavelength measurements and the opacity model: November 2014

- Submit Master's Thesis: December 2014

References

- [1] D. R. DeBoer, P. G. Steffes, Laboratory Measurements of the Microwave Properties of H₂S under Simulated Jovian Conditions with an Application to Neptune, *Icarus* 109 (2) (1993) 352–366.
- [2] K. Devaraj, The Centimeter- and Millimeter-Wavelength Ammonia Absorption Spectra Under Jovian Conditions, Ph.D. thesis, Georgia Institute of Technology (December 2011).
- [3] K. Devaraj, P. G. Steffes, The Georgia Tech millimeter-wavelength measurement system and some applications to the study of planetary atmospheres, *Radio Science* 46 (2) (2011) n/a–n/a.
URL <http://dx.doi.org/10.1029/2010RS004433>
- [4] A. K. Fahd, P. G. Steffes, Laboratory measurements of the microwave and millimeter-wave opacity of gaseous sulfur dioxide (SO₂) under simulated conditions for the Venus atmosphere, *Icarus* 97 (2) (1991) 200–210.
URL [http://dx.doi.org/10.1016/0019-1035\(92\)90128-T](http://dx.doi.org/10.1016/0019-1035(92)90128-T)
- [5] T. R. Hanley, P. G. Steffes, A high-sensitivity laboratory system for measuring the microwave properties of gases under simulated conditions for planetary atmospheres, *Radio Science* 42 (6) (2007) n/a–n/a.
URL <http://dx.doi.org/10.1029/2007RS003693>
- [6] G. L. Matthael, E. Jones, Microwave filters, impedance matching networks and coupling structures, McGraw-Hill, New York, 1980.

- [7] H. Sagawa, Terahertz remote sensing of the Venusian atmosphere: Observations Using the Nobeyama Millimeter Array, *Journal of the National Institute of Information and Communications Technology* 55 (2008) 149–157.
- [8] P. Steffes, C. Barisich, Laboratory measurements of the 3.7-20 cm wavelength opacity of sulfur dioxide and carbon dioxide under simulated conditions for the deep atmosphere of Venus, in: *Bulletin of the American Astronomical Society*, vol. 44, Reno, NV, 2012, p. 241, presented at the 44th Annual Meeting of the Division for Planetary Sciences of the American Astronomical Society.
- [9] P. Steffes, P. Shahan, Models of the centimeter-wavelength of sulfur dioxide and carbon dioxide based on laboratory measurements conducted under simulated conditions for the deep atmosphere of Venus, in: *Bulletin of the American Astronomical Society*, vol. 45, Denver, CO, 2013, p. 57, presented at the 45th Annual Meeting of the Division for Planetary Sciences of the American Astronomical Society.
- [10] S. H. Suleiman, Microwave effects of gaseous sulfur dioxide (SO_2) in the atmospheres of Venus and Earth, Ph.D. thesis, Georgia Institute of Technology (May 1997).