I. INTRODUCTION AND SUMMARY

Radio absorptivity data for planetary atmospheres obtained from spacecraft radio occultation experiments, entry probe radio signal absorption measurements, and earth-based or spacecraft-based radio astronomical (emission) observations can be used to infer abundances of microwave absorbing constituents in those atmospheres, as long as reliable information regarding the microwave absorbing properties of potential constituents is available. The use of theoretically-derived microwave absorption properties for such atmospheric constituents, or the use of laboratory measurements of such properties taken under environmental conditions that are significantly different than those of the planetary atmosphere being studied, often leads to significant misinterpretation of available opacity data. Additionally, even if laboratory measurements have previously been conducted, improvements in the sensitivity of new space-based and earth-based microwave sensors may require higher precision laboratory measurements to achieve their basic science goals.

With improved laboratory capability, it has been possible to achieve a wider range of environmental conditions in the laboratory, which are similar to those actually being probed by microwave sensors. For example, an upgrade to one of our laboratory systems was completed recently by Steffes et al. (2014) under our predecessor Planetary Atmospheres grant (NNX11AD66G, 1/15/11-1/14/15), and was used to conduct measurements of the 3.7-20 cm opacity of sulfur dioxide in a carbon dioxide atmosphere under simulated conditions for the Venus boundary layer (92 Bars pressure). The 300 data points taken using this new system and a new millimeter-wavelength system, which measured the 2-4 mm opacity of sulfur dioxide in a carbon dioxide atmosphere under simulated conditions for the upper troposphere of Venus, have been used to verify models for SO_2 opacity which will allow for accurate retrieval of spatial and temporal variations in SO_2 abundances from both centimeter-wavelength and millimeter-wavelength observations of the Venus atmosphere.

The recognition of the need to make such laboratory measurements of simulated planetary atmospheres over a range of temperatures and pressures which correspond to the altitudes probed by radio occultation experiments, entry probe radio link experiments, and radio astronomical observations, and over a range of frequencies which correspond to those used in both spacecraft experiments and in radio astronomical observations, has led to the development of a facility at Georgia Tech which is capable of making such measurements. It is the goal of this investigation to conduct such measurements *and* to apply the results to a wide range of planetary observations, both spacecraft and earth-based, in order to determine the identity and abundance profiles of constituents in those planetary atmospheres.

In the 3-year program proposed, key activities will include applying results from our recently-completed laboratory measurements of the microwave and millimeter-wave properties of sulfur dioxide to recently-completed observations of Venus conducted by our group at the NRAO Very Large Array (3.6 cm images) and at the Combined Array for Millimeter Astronomy (CARMA, 2.6-3.0 mm images), and to recently-published observations of Venus conducted with the Atacama Large Millimeter/submillimeter Array (ALMA). Additionally, new laboratory measurements of the millimeter-wavelength absorption of gaseous sulfuric acid will be conducted over an extended range of frequencies (30-40 GHz, or 7.5-10mm, and 75-150 GHz, or

2-4 mm) under simulated conditions for the atmosphere of Venus. While measurements have been made of a number of the over 42,000 centimeter-, millimeter-, and submillimeter-wavelength lines of sulfuric acid vapor (see, e.g., Cohen and Drouin, 2013), no laboratory measurements of the millimeter-wavelength continuum spectrum of sulfuric acid vapor have ever been conducted. Since the weighting functions at these wavelengths generally peak from just below the lower cloud base to the top of the middle cloud (pressures 0.3-2 Bars), measurements will be taken in that pressure range. These measurements will make it possible to interpret the source of variations in Venus millimeter-wavelength emissions reported in previous radio astronomical observations and those recently completed, by using a new radiative transfer model which will employ our new lab measurements. The 7.5-10 mm measurements will also directly support Ka-Band radio occultation measurements, which will likely be conducted in the next generation of Venus missions. These measurements will be conducted using a new millimeter-wavelength laboratory system specifically developed for measurement of sulfuric acid vapor under our predecessor grant (NNX11AD66G, 1/15/11-1/14/15).

II. RELEVANCE TO THE SOLAR SYSTEM WORKINGS PROGRAM

An aggressive program of laboratory measurements of the millimeter-wave properties of gaseous sulfuric acid under simulated Venus conditions is proposed. These measurements are directly relevant to the Solar System Workings Program in that when they are applied to our radiative transfer models and to observations of Venus from both earth-based and spacecraft-based instruments, important new insights into the composition and dynamics of the Venus atmosphere will be obtained.

Specifically, the millimeter-wavelength radiative transfer studies proposed (employing our recently completed laboratory measurements of sulfur dioxide pertinent to the atmosphere of Venus and the proposed measurements of gaseous sulfuric acid) will be applied to earth-based millimeter-wavelength observations of Venus so as to provide planetary maps of sulfuric acid vapor and sulfur dioxide abundance at and immediately below the main cloud layer. Interpretation of such observations will complement the study of the long-term variations of SO_2 abundance at the 70 km altitude level measured over the duration of the Pioneer-Venus and Venus Express missions using the UV instruments, and give insight into the processes driving this noteworthy temporal variation. Such work can directly support proposed Discovery-Class missions to Venus by providing contextual images of cloud-related gases, and by enabling the interpretation of Ka-Band (9.2 mm-wavelength) radio occultation experiments, which are being considered by several proposing teams. Moreover, the new laboratory measurements of the millimeter-wavelength properties of sulfur-bearing gases under simulated Venus conditions and their application to currently available millimeter-wavelength maps of Venus using our radiative transfer model will help *"Determine the abundances and altitude profiles of reactive atmospheric species (OCS, H_2S, SO_2, H_2SO_4, S_n, HCl, HF, ClO_2, and Cl_2), greenhouse gases, H_2O, and other condensables, in order to characterize sources of chemical disequilibrium in the atmosphere and to understand influences on the current climate."* which is identified as a priority investigation in *Goals, Objectives, and Investigations for Venus Exploration: 2014* (VEXAG, 2014).

III. RECENTLY COMPLETED LABORATORY MEASUREMENTS AND OBSERVATIONS: *CENTIMETER-WAVELENGTH LABORATORY MEASUREMENTS OF CARBON DIOXIDE AND SULFUR DIOXIDE UNDER SIMULATED CONDITIONS FOR THE DEEP ATMOSPHERE OF VENUS*

It is well understood that the microwave emission spectrum of Venus reflects the abundance and distribution of constituents such as carbon dioxide, sulfur dioxide, and sulfuric acid vapor (see, e.g., Steffes et al., 1990), but there are a number of factors that limit the accuracy of this approach for microwave remote sensing of these constituents. The most critical of these is the knowledge of the microwave absorption properties of these constituents under Venus atmospheric conditions. While the *centimeter-wavelength* absorption properties of both gaseous sulfuric acid vapor and sulfur dioxide in a carbon dioxide atmosphere have been measured and modeled at pressures up to 6 bars (Kolodner et al., 1998, Suleiman et al., 1996, Fahd and Steffes, 1992), no measurements of the centimeter-wavelength properties of any Venus atmospheric constituent had been conducted under conditions characteristic of the deep atmosphere (pressures from 10-92 Bars and temperatures from 400-700 K), excepting a single measurement campaign conducted at a single wavelength (3.2 cm) over 40 years ago (Ho et al., 1966). At altitudes below 35 km, H_2SO_4 thermally dissociates, forming H_2O and SO_3, both of which exhibit very 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.

Microwave observations of Venus were conducted in 1996 at 4 wavelengths using the NRAO Very Large Array (Butler *et al*., 2001). Maps of emission from Venus were made at two of the wavelengths (1.3 cm and 2.0 cm), which indicated dark (~3%) polar regions consistent with increased sulfuric acid vapor abundance due to vaporization of cloud condensate from the downwelling characteristic of Hadley cell circulation (Jenkins *et al.*, 2002). Over the disk of Venus, the weighting functions at these wavelengths peak well above the surface or boundary layer (Jenkins *et al.*, 2002). Even at the disk center (nadir), with the deepest possible weighting functions, the emission at wavelengths of 2 cm and shorter largely originates from altitudes above the boundary layer, which exists from 0-10 km. At 3.6 cm, emission from both the boundary layer and surface are present. Supported by our predecessor grant (NNX11AD66G, 1/15/11-1/14/15), (Devaraj (2011) made maps of the 3.6 cm emission from Venus based both on the 1996 observations (Butler *et al.*, 2001) and from subsequent observations conducted in 2009 from the NRAO Very Large Array. Since variations in 3.6 cm emission are due both to variations in surface emissivity and potentially from variability in the abundance of SO_2 in the boundary layer, accurate interpretation of such data requires accurate models of the microwave opacity of constituents in the boundary layer (Figure 3).

Under the predecessor grant (NNX11AD66G, 1/15/11-1/14/15), we conducted laboratory measurements of the microwave properties of SO_2 and CO_2 at wavelengths from 3.7-20 cm under simulated conditions for the deep atmosphere of Venus, using a new high-pressure system. Results from this measurement campaign conducted at temperatures from 430 K to 560 K and at pressures up to 92 Bars indicate that the model for the centimeter-wavelength opacity of pure CO_2 (developed over 40 years ago -- Ho et al., 1966 – see Figure 1), is valid over the entire centimeter-wavelength range under simulated conditions for the deep atmosphere of Venus. Additionally, the laboratory results (example in Figure 2) indicate that the models for the centimeter-wavelength opacity of SO_2 in a CO_2 atmosphere from Suleiman et al. (1996) and from Fahd and Steffes (1992) can reliably be used under conditions of the deep atmosphere of Venus. (These results were submitted to the journal *Icarus* in June 2014: Steffes *et al.*, 2014.)

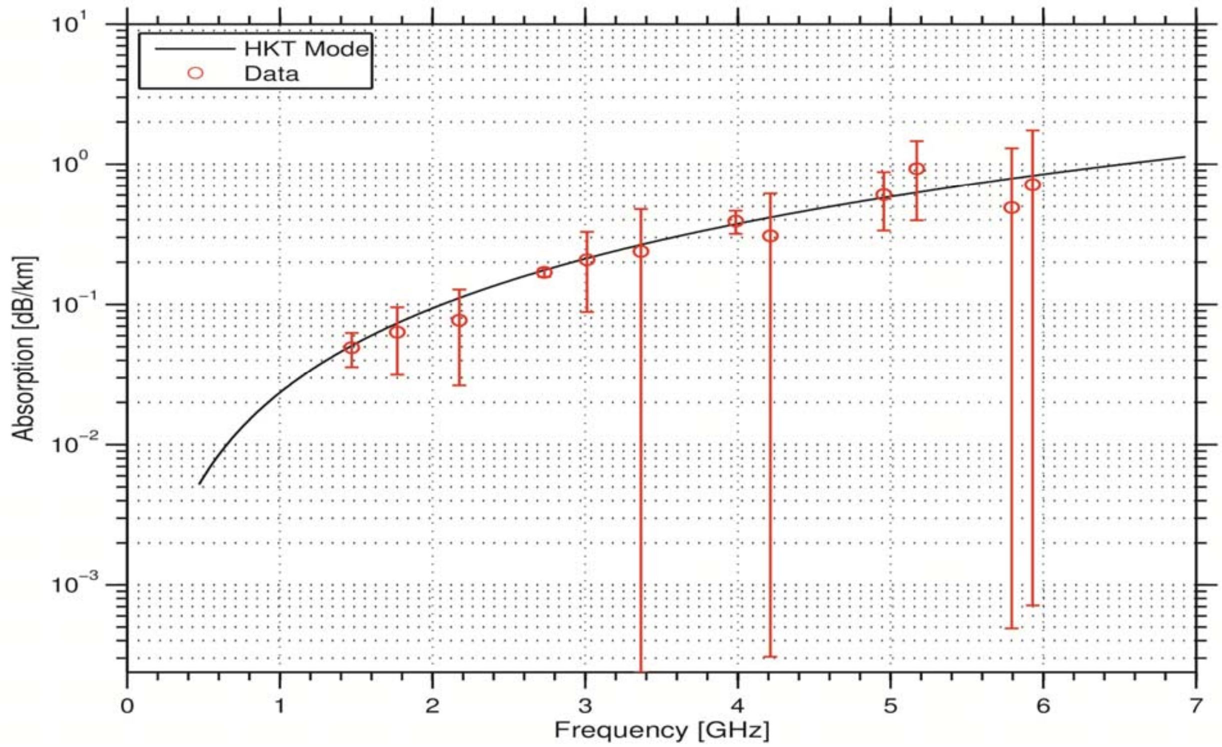

Figure 1: Measured microwave opacity of pure CO_2 at pressure 78.05 bars and 495.4 K compared with model from Ho et al. (1966).

When our radiative transfer model for Venus (using these models for constituent opacity and a nominal abundance of 75ppm for SO_2 from the boundary layer up to the base of the clouds) is used as a reference, the residual brightness variations shown in Figure 3, map to deep atmospheric abundances variations of SO_2 of up to 60 ppm in the boundary layer. However, since the statistical variation of the maps using the original VLA configuration is relatively large (standard deviation of 3.6 cm emission measured across Venus disk is approximately 2 K), higher precision measurements, such as could be obtained by a spacecraft-borne 3-cm radiometer (proposed by some previous Discovery class missions) or by new observations with the more sensitive NRAO-EVLA (Expanded Very Large Array) will provide improved sensitivity at this wavelength and can be used to detect potential sources of elevated SO_2 in the boundary layer.

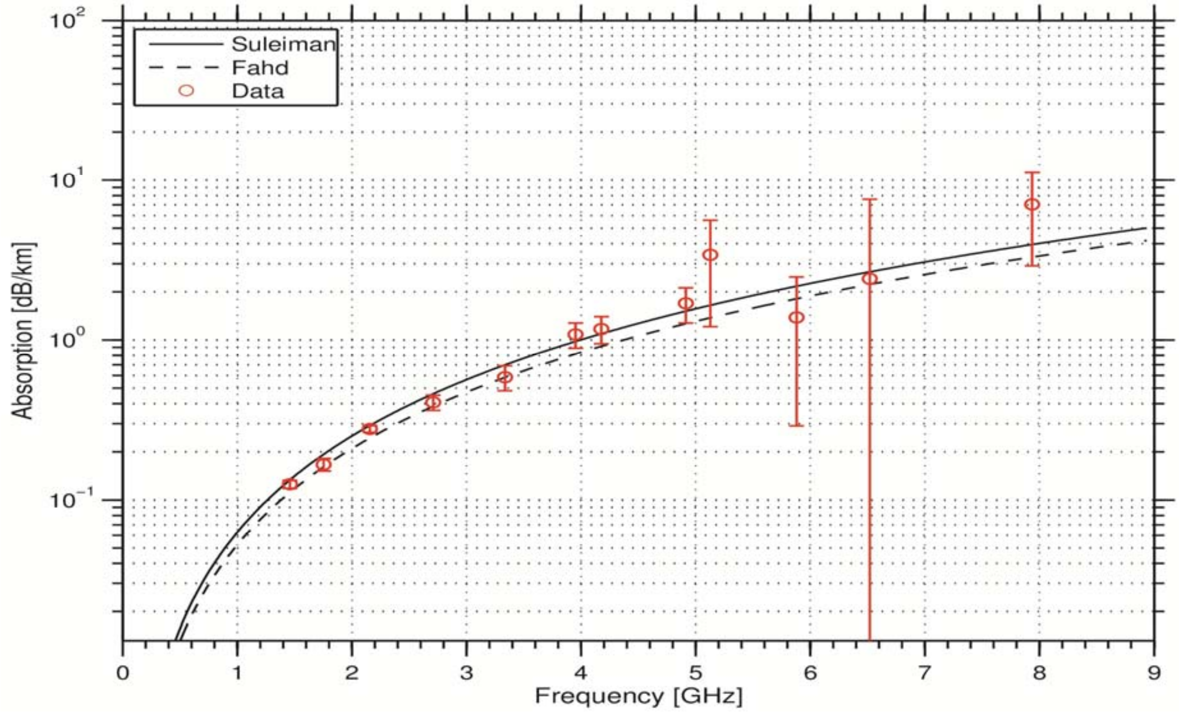

Figure 2: Measured microwave opacity of SO_2 (0.250 Bars, or 0.240% by mole fraction, corrected for compressibility) in a CO_2 atmosphere at 435.3 K and 92.002 Bars pressure compared with models from Suleiman et al. (1996) and from Fahd and Steffes (1992).

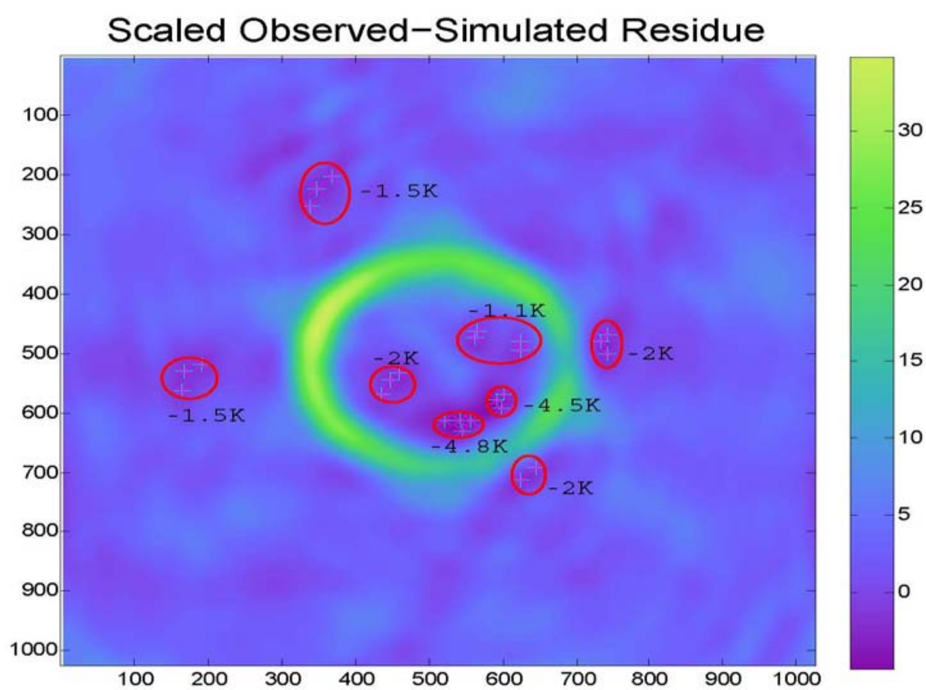

Figure 3: Residual map of microwave Venus microwave emissivity at 3.6 cm (8.4 GHz). The residual is relative to a modeled atmosphere containing 75 ppm of SO_2 in a CO_2 atmosphere. Variations in the surface emissivity measured at the 12.6 cm wavelength by the Magellan mission have been extrapolated to 3.6 cm and subtracted from the emission.

IV. PROPOSED LABORATORY MEASUREMENTS AND APPLICATION TO OBSERVATIONS: *LABORATORY MEASUREMENTS OF THE MILLIMETER-WAVELENGTH OPACITY SPECTRUM OF GASEOUS SULFURIC ACID UNDER SIMULATED CONDITIONS FOR THE ATMOSPHERE OF VENUS*

For over 30 years, sulfuric acid vapor (H_2SO_4) has been recognized as a major source of the microwave absorption in the atmosphere of Venus (Steffes and Eshleman, 1982). Through radio occultation measurements from both the Pioneer-Venus and Magellan, it has been possible to retrieve abundance profiles of gaseous H_2SO_4 in the atmosphere of Venus (Jenkins and Steffes, 1991 and Jenkins *et al.*, 1994). Laboratory measurements of the *centimeter-wavelength* opacity of gaseous H_2SO_4 in a CO_2 atmosphere (Kolodner and Steffes, 1998) dramatically increased the precision of retrievals from both radio occultation experiments (conducted at 3.6 and 13 cm) and from radio emission measurements conducted at 1.3 and 2.0 cm (Jenkins *et al.*, 2002). Recently, observations of Venus with the Nobeyama millimeter-wave array conducted at 103 GHz (~3mm) showed substantial variation (~25%) in the millimeter-wave brightness with position on the disk (Sagawa, 2008). While maps of the 1.3 and 2.0 cm emission from Venus have indicated dark (~3%) polar regions consistent with increased sulfuric acid vapor abundance due to vaporization of cloud condensate from the downwelling characteristic of Hadley cell circulation (Jenkins *et al.,* 2002), the 3 mm maps show much stronger variations over a range of different locations, with some indication of diurnal variation. de Pater *et al.* (1991a) also reported significant variations (10%) in the 2.6 mm emission maps of Venus made with the Hat Creek Interferometer. Recent maps of Venus made by our group from 100-116 GHz (2.6-3.0mm) under our predecessor grant (NNX11AD66G, 1/15/11-1/14/15) using the CARMA (Combined Array for Research in Millimeter-wave Astronomy) show the same types of variation. (See, e.g., Figure 4.)

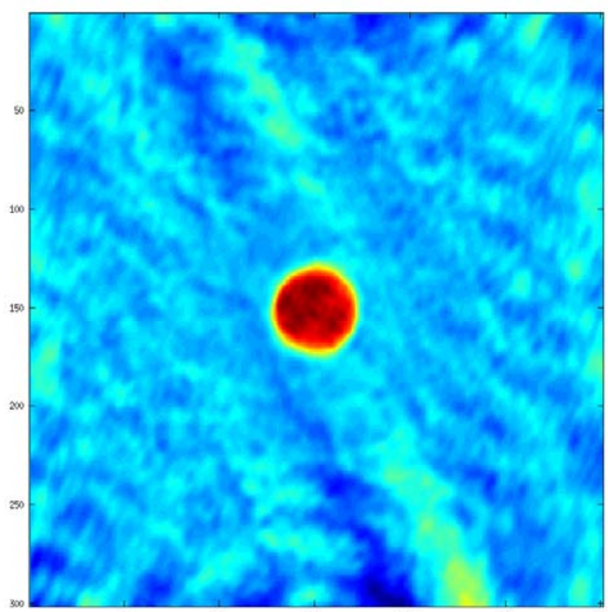

Figure 4: 100.7 GHz Venus emission residual as measured using the Combined Array for Research in Millimeter-Wave Astronomy (CARMA) array.

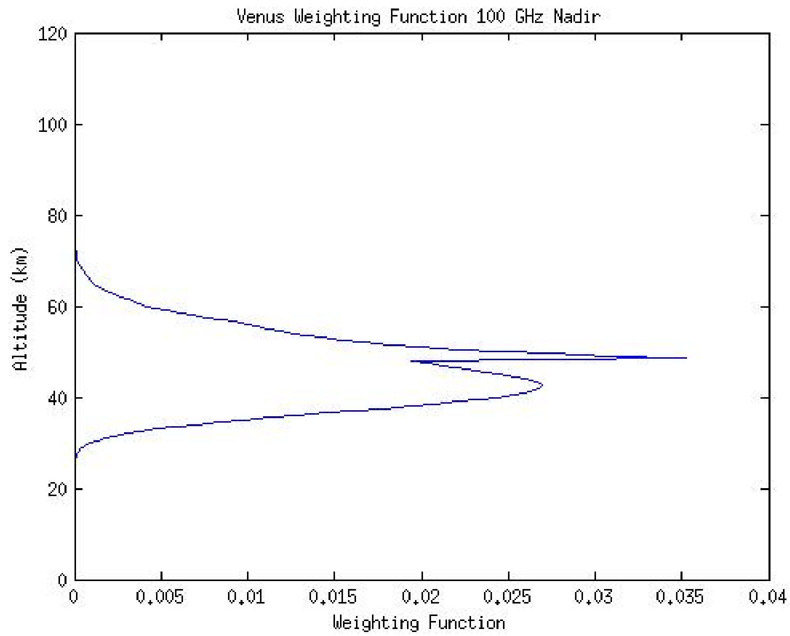

Figure 5: Altitude weighting function for Venus emission at 100 GHz computed using Georgia Tech Venus Radiative Transfer Model (GT-VRTM) developed under our predecessor grant.

Sagawa (2008) attributes the Venus millimeter-wavelength continuum brightness variations to spatial variations in the abundances of both gaseous H_2SO_4 and SO_2 in a range of altitudes from just below the lower cloud base to the top of the middle cloud (pressures 0.3-2 Bars). This is consistent with the weighting functions our (Georgia Tech) Venus radiative transfer model (see Figure 5). However his attribution involves use of models for the millimeter-wavelength opacities of these constituents which were extrapolated from previous centimeter-wavelength measurements. Additionally, Sagawa has suggested that the effects of the two constituents could be distinguished based on differences in frequency (wavelength) dependencies of the millimeter-wave absorption from both constituents, but those wavelength dependencies were uncertain. Under our predecessor grant (NNX11AD66G, 1/15/11-1/14/15), we recently completed measurements of the millimeter-wave absorption from SO_2 at these pressures under simulated Venus conditions (CO_2 atmosphere with temperatures from 307-343 K). One example of our laboratory results is in Figures 6 (below). Our laboratory measurements conducted in the 2-4 mm wavelength range verify the accuracy of both the Fahd and Steffes (1992) and Suleiman et al. (1996) models for use at millimeter-wavelengths. [Note that these laboratory results are part of a Master's thesis being completed by graduate student Amadeo Bellotti (Bellotti, 2014) and will also be the basis for a paper being prepared for submission to *Icarus* (Bellotti and Steffes, 2014).]

Determination of the millimeter-wavelength absorption from gaseous H_2SO_4 is more speculative. While measurements have been made of a number of the line center *frequencies* of the over 42,000 centimeter-, millimeter-, and submillimeter-wavelength lines of sulfuric acid vapor (see, e.g., Cohen and Drouin, 2013), a much smaller number of line *intensities* have ever been directly measured. Moreover, no laboratory measurements of the millimeter-wavelength continuum spectrum of sulfuric acid vapor broadened by carbon dioxide have ever been conducted.

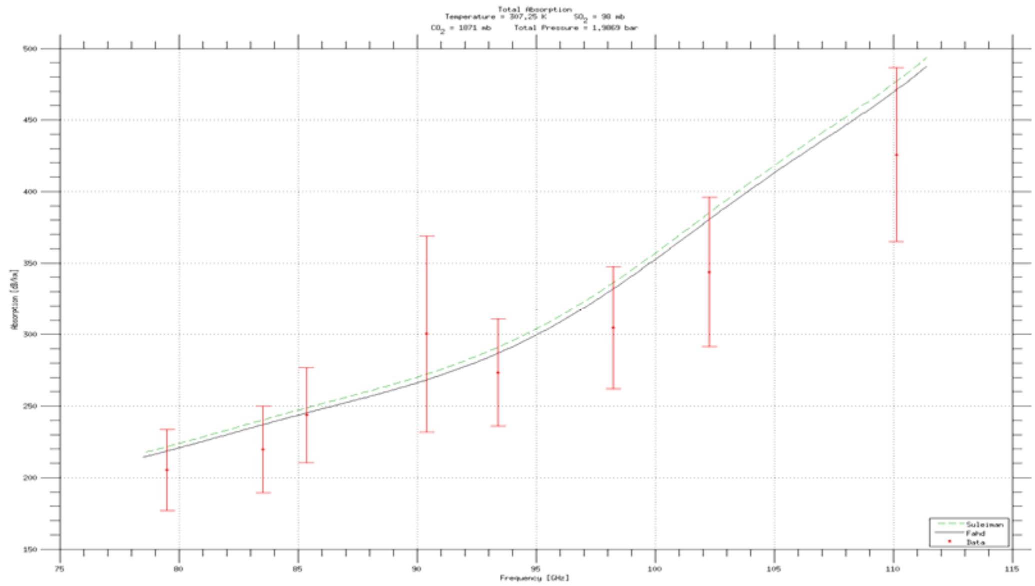

Figure 6: Measured absorptivity from SO_2 (partial pressure 98 mBars) in a CO_2 atmosphere (total pressure 1.87 Bars) at 307 K in the 78-110 GHz (2.7-3.8 mm) range. Also shown are calculated opacities from models by Fahd and Steffes (1992) and Suleiman et al. (1996). This profile is one of several measured from 75-150 GHz (2-4 mm) and from 307-345 K at pressures from 0.05-2 Bars.