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> LABORATORY MEASUREMENTS OF MICROWAVE AND MILLIMETER-WAVE PROPERTIES OF PLANETARY ATMOSPHERIC CONSTITUENTS

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ABSTRACT

Accurate data on microwave and millimeter-wave properties of potential planetary atmospheric constituents is critical for the proper interpretation of radio occultation measurements, and of radio astronomical observations of both continuum and spectral line emissions. Such data is also needed to correct for atmospheric effects on radar studies of surface reflectivity. Since the refractive and absorptive properties of atmospheric constituents often vary drastically from theoretically-predicted profiles, especially under the extreme conditions characteristic of planetary atmospheres, laboratory measurements under simulated planetary conditions are required.

This paper reviews the instrumentation and techniques used for laboratory measurement of the refractivity and absorptivity of atmospheric constituents at wavelengths longward of 1 mm, under simulated planetary conditions (temperature, pressure, and broadening gases). Techniques for measuring both gases and condensates are considered. Also reviewed are the relative accuracies of the various techniques. We conclude by reviewing laboratory measurements which have already been made, and highlight additional measurements which are needed for interpretation of data from Venus and the outer planets.

I. INTRODUCTION

Radio absorptivity data for planetary atmospheres obtained from spacecraft radio occultation experiments and earth-based radio astronomical observations can be used to infer abundances of microwave absorbing atmospheric 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 laboratory measurements of such properties under environmental conditions which are significantly different than those of the planetary

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atmosphere being studied, often leads to significant misinterpretation of available opacity data. For example, results obtained for the microwave opacity from gaseous H₂SO₄, under simulated Venus conditions showed that not only was the opacity from H₂SO₄ much greater than theoretically predicted, but that its frequency (wavelength) dependence was far different than that theoretically predicted (Steffes, 1985 and Steffes, 1986). Subsequent measurements made by Steffes and Jenkins (1987), showed that the microwave opacity of gaseous ammonia (NH₃) under simulated Jovian conditions did agree with theoretical predictions to within their experimental accuracy at wavelengths longward of 1.3 cm. However, work performed by Joiner et al. (1989) has shown that laboratory measurements of the millimeter-wave opacity of ammonia between 7.5 mm and 9.3 mm and also at the 3.2 mm wavelength require a different lineshape to be used in the theoretical prediction for millimeter-wave ammonia opacity than had been The recognition of the need to make such laboratory previously used. measurements of simulated planetary atmospheres over a range of temperatures and pressures which correspond to the altitudes probed by both radio occultation experiments and radio astronomical observations, and over a range of frequencies which correspond to those used in both radio occultation experiments and radio astronomical observations, has led to the development of facilities at Georgia Tech and at other institutions which are capable of making such measurements.

This paper reviews the instrumentation and techniques used for laboratory measurement of the refractivity and absorptivity of atmospheric constituents at wavelengths longward of 1 mm, under simulated planetary conditions (temperature, pressure, and broadening gases). Techniques for measuring both gases and condensates are considered. Also reviewed are the relative accuracies of the various techniques. We conclude by reviewing laboratory measurements which have already been made, and highlight additional measurements which are needed for interpretation of data from Venus and the outer planets.

II. INSTRUMENTATION AND MEASUREMENT TECHNIQUES

A large number of measurement techniques are used for characterizing the refractivity and absorptivity of gases and condensates at microwave and millimeter-wavelengths. At the shorter millimeter-wavelengths (near 1 mm), the techniques resemble the IR/optical spectroscopic techniques described by other authors. At the longer microwave wavelengths ($\lambda > 1$ cm), techniques involving

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RF (radio frequency) components are employed.

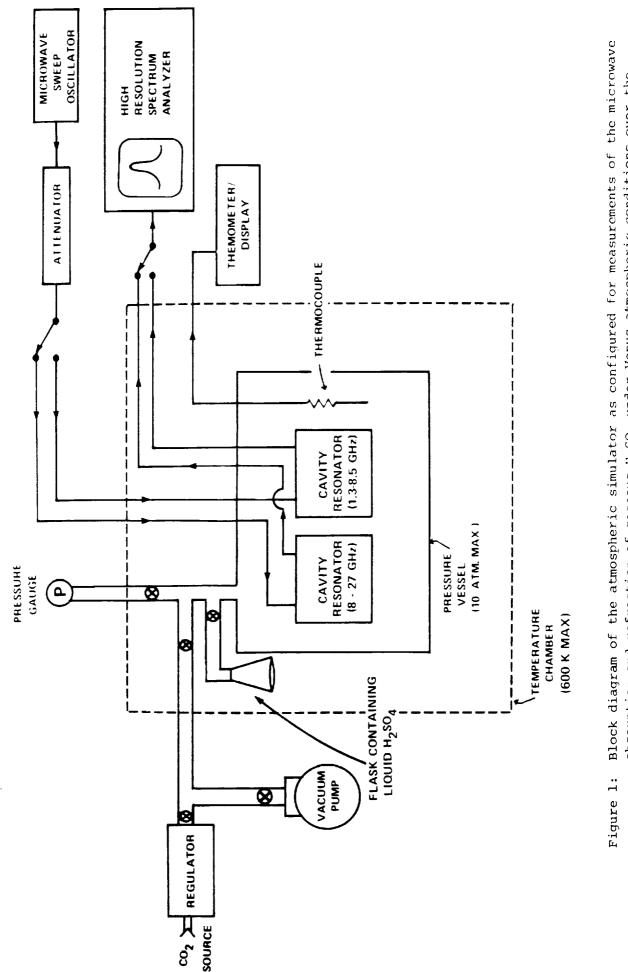
A. <u>Absorptivity Measurements at Wavelengths Longward of 1 cm</u>

At wavelengths longward of 1 cm, the two major techniques for inferring planetary atmospheric opacity and refractivity are spacecraft radio occultation experiments and earth-based radio emission measurements. At these wavelengths, the vast majority of measured opacity is due to atmospheric gases at pressures at or above 1 Bar. Measurement of the microwave absorption and refraction properties of such gases is most often accomplished with cylindrical cavity resonators. Figure 1 (from Steffes, 1986) and Figure 2 (from Steffes and Jenkins, 1987) show measurement systems designed to measure microwave absorption and refraction properties of atmospheric gases under simulated conditions for the Venus atmosphere (Figure 1) and the atmospheres of the outer planets (Figure 2).

The approach used to measure the microwave absorptivity of gaseous H_2SO_4 in a CO_2 atmosphere can be seen in Figure 1. The absorptivity is measured by observing the effects of the introduced gas mixture on the Q, or quality factor, of two cavity resonators at particular resonances from 1.34 GHz to 23.6 GHz. The changes in the Q of the resonances which are induced by the introduction of an absorbing gas mixture can be monitored by the high resolution microwave spectrum analyzer, since Q is simply the ratio of the cavity resonant frequency to its half-power bandwidth. For relatively low-loss gas mixtures, the relation between the absorptivity of the gas mixture and its effect on the Q of a resonance is straightforward:

$$\alpha \simeq (Q^{-1} - Q^{-1}) \pi/\lambda \tag{1}$$

where α is absorptivity of the gas mixture in Nepers km⁻¹. (Note, for example, that an attenuation constant or absorption coefficient or absorptivity of 1 Neper km⁻¹ = 2 optical depths per km (or km⁻¹) = 8.686 dB km⁻¹, where the first notation is the natural form used in electrical engineering, the second is the usual form in physics and astronomy, and the third is the common (logarithmic) form. The third form is often used in order to avoid a possible factor-of-two ambiguity in meaning.) Q_L is the quality factor of the cavity resonator when the gas mixture is present, Q_C is the quality factor of the cavity resonator in a vacuum, and λ is the wavelength (in km) of the test signal in the gas mixture.



absorption and refraction of gaseous $H_2^{SO_4}$ under Venus atmospheric conditions over the 1.2-22.3 cm wavelength range.

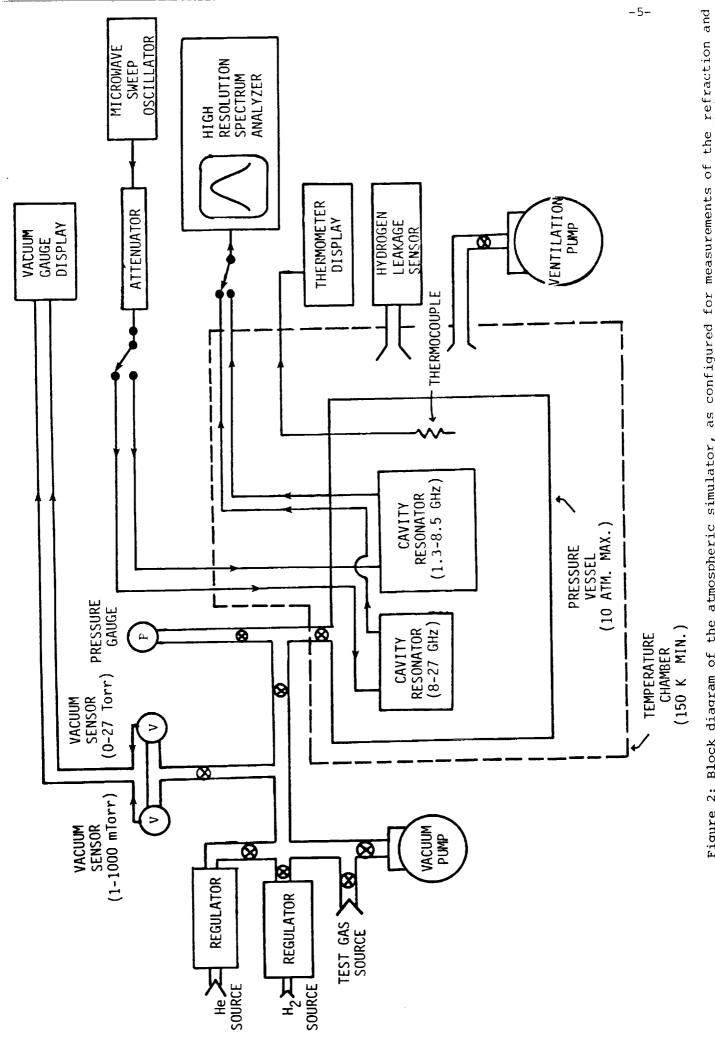


Figure 2: Block diagram of the atmospheric simulator, as configured for measurements of the refraction and microwave absorption of test gases $(NH_3, CH_4, and H_2^0)$ under simulated Jovian conditions.

In order to obtain a gas mixture with a sufficient amount of H_2SO_4 vapor so that the microwave absorption is detectable, the system must be operated at temperatures exceeding 450 K. While this is suboptimal in that the temperatures at altitudes from 35 to 50 km (where both radio occultation and radio astronomical experiments have detected microwave opacity) range from 350 to 450 K, temperature dependencies measured for similar gases (such as SO₂) can be used to estimate temperature effects in that range. In order to infer H_2SO_4 vapor pressure, the volume of liquid sulfuric acid which is vaporized to generate the gaseous H_2SO_4 is determined to a high accuracy (up to ± 0.005 ml). It is then possible to compute the partial pressure of gaseous H₂SO₄ using the ideal gas equation, the measured change in liquid volume, and published densities for H_2SO_4 liquid. However, since gaseous H_2SO_4 can dissociate to form gaseous H_2O and SO_3 which have relatively low microwave opacity when compared with gaseous H_2SO_4 , an accurate estimate of the "dissociation factor" is necessary in order accurately estimate the H_2SO_4 abundance, and therefore the relationship between abundance and absorptivity. Recently, Fahd and Steffes (1989) have measured this Initially, a vacuum is drawn in the pressure vessel dissociation factor. containing the microwave cavity resonator, and the bandwidth and center frequency of the resonances are then measured. For this experiment, resonances at 1.34 GHz (22.3 cm) 2.24 GHz (13.4 cm), 8.42 GHz (3.6 cm), 13.23 GHz (2.26 cm), 21.63 GHz (1.38), and 23.64 GHz (1.27 cm) were used. A valve is then opened which allows the sulfuric acid vapor eluting from the flask to fill the pressure vessel (0.031 cubic meters of open volume with resonator in place) and reach vapor pressure equilibrium with the liquid H_2SO_4 .

As H_2SO_4 vapor fills the chamber, changes in the resonance center frequency are observed. These changes are related to the H_2SO_4 vapor abundance. After equilibrium is reached, the valve to the reservoir flask is then closed, and CO_2 is admitted to the chamber containing the H_2SO_4 vapor. For this experiment, a total pressure of 6 atm was used. The bandwidth of each response is then measured and compared with its value when the chamber was evacuated in order to determine the absorptivity of the CO_2/H_2SO_4 gas mixture at 6 atm total pressure. The total pressure is then reduced by venting, and the bandwidths are again measured. Subsequent measurements are likewise made at lower pressures in order to determine absorptivities at those pressures. The pressure vessel is then evacuated and the bandwidths again measured so as to assure no variation (either

due to thermal shift or chemical reaction) of the Q's of the evacuated resonators has occurred. Note that this approach has the advantage that the same gas mixture is used for the absorptivity measurements at the various pressures. Thus, even though some uncertainty may exist as to the mixing ratio of the initial mixtue, the mixing ratios at all pressures are the same, and thus the uncertainty for any derived pressure <u>dependence</u> is due only to the accuracy limits of the absorptivity measurements, and not to uncertainty in the mixing ratio. Similarly, measurements of the frequency <u>dependence</u> of the absorptivity from the gas mixture are likewise immune to mixing ratio uncertainty, as long as foreign-gas broadening predominates.

Measurements have also been made of the absorptive properties of several gases under simulated conditions for the outer planets, using the system in Figure 2. The first experiment involved gaseous NH₃.

In order to obtain a gas mixture with a sufficient amount of gaseous NH_3 so that microwave absorption is detectable using our system, temperatures at or above 170 K must be used. (This limit is set by the saturation vapor pressures for ammonia and by the sensitivity of our measurement system.) While this covers most of the temperature range in the Jupiter atmosphere over which radio occultation and radio astronomical experiments have detected microwave opacity (140-300 K), it is somewhat above the temperature range over which microwave opacity has been detected at Saturn. However, the measured temperature dependencies can be used to extrapolate to those temperatures. In order to conduct the required measurements, the pressure vessel and its microwave resonators must first be cooled to the desired temperature.

After thermal stability is reached, which can be monitored using both the temperature sensors and the resonant frequencies of the system, a vacuum is drawn in the pressure vessel containing the resonators, and the bandwidth and center frequency of each of resonances is then measured. For this experiment (absorption from NH₃), resonances at 1.34 GHz (22.3 cm), 2.25 GHz (13.3 cm), 8.53 GHz (3.52 cm), 13.3 GHz (2.26 cm), and 21.7 GHz (1.38 cm) were used. A valve is then opened which allows the ammonia gas to enter the chamber. Measurements of the gaseous NH₃ pressure were made with the high accuracy thermocouple vacuum gauge tubes which are shown in Figure 2. Next, 5.4 atm of hydrogen (H₂) and 0.6

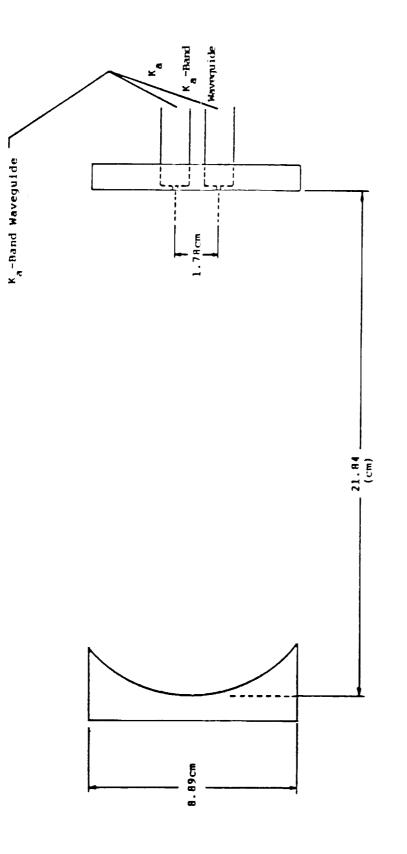
atm of helium (He) are added. These gases are admitted to the chamber at a sufficiently slow rate so as not to significantly affect the temperature within the chamber. The bandwidth of each resonance is then measured and compared with its value when the chamber was evacuated in order to determine the absorptivity of the gas mixture at 6 atm total pressure. The total pressure is then reduced by venting to 4 atm, and the bandwidths are again measured.

As before, this approach has the advantage that the same gas mixture is used for the absorptivity measurements at the various pressures. Thus, even though some small uncertainty may exist as to the mixing ratio of the initial mixture, the mixing ratios at all pressures are the same.

B. Absorptivity Measurements at Wavelengths Between 1 mm and 1 cm

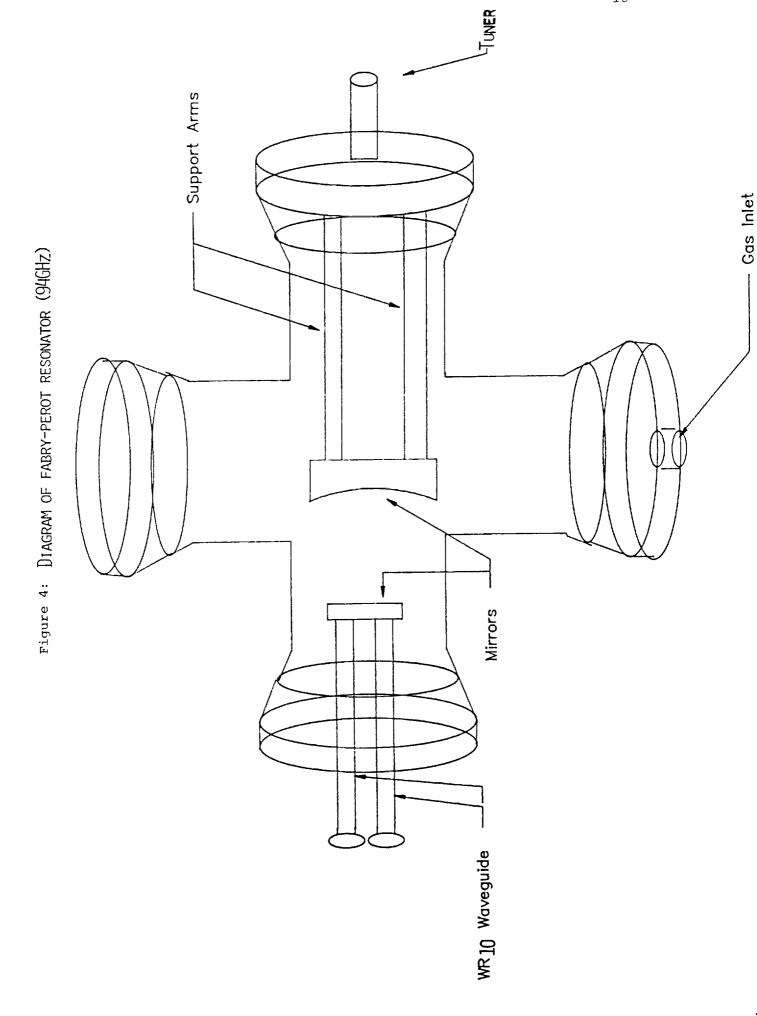
While the techniques for measuring millimeter-wave absorptivity are similar to those used at longer wavelengths, the cylindrical resonators used at wavelengths longward of 1 cm become ineffective at the shorter wavelengths. Shortward of 1 cm, cylindrical resonators become extremely small, resulting in a very low quality factor (Q) and making it difficult to couple energy in and out of the resonator. An alternative approach is the semi-confocal Fabry-Perot resonator shown in Figure 3. The resonator shown in Figure 3 has several bandpass resonances in the range from 30-40 GHz with quality factors around 8000. A similar resonator which operates at 94 GHz with a Q of over 30,000 is shown in Figure 4. The system used to measure the 94 GHz absorptivity of NH₃ in a H₂/He atmosphere is shown in Figure 5. Note the use of a premixed, constituent analyzed, hydrogen/helium/ammonia atmosphere with a mixing ratio accuracy of better than \pm 2% of its value (e.g., [1.85 \pm 0.04] % of NH₃).

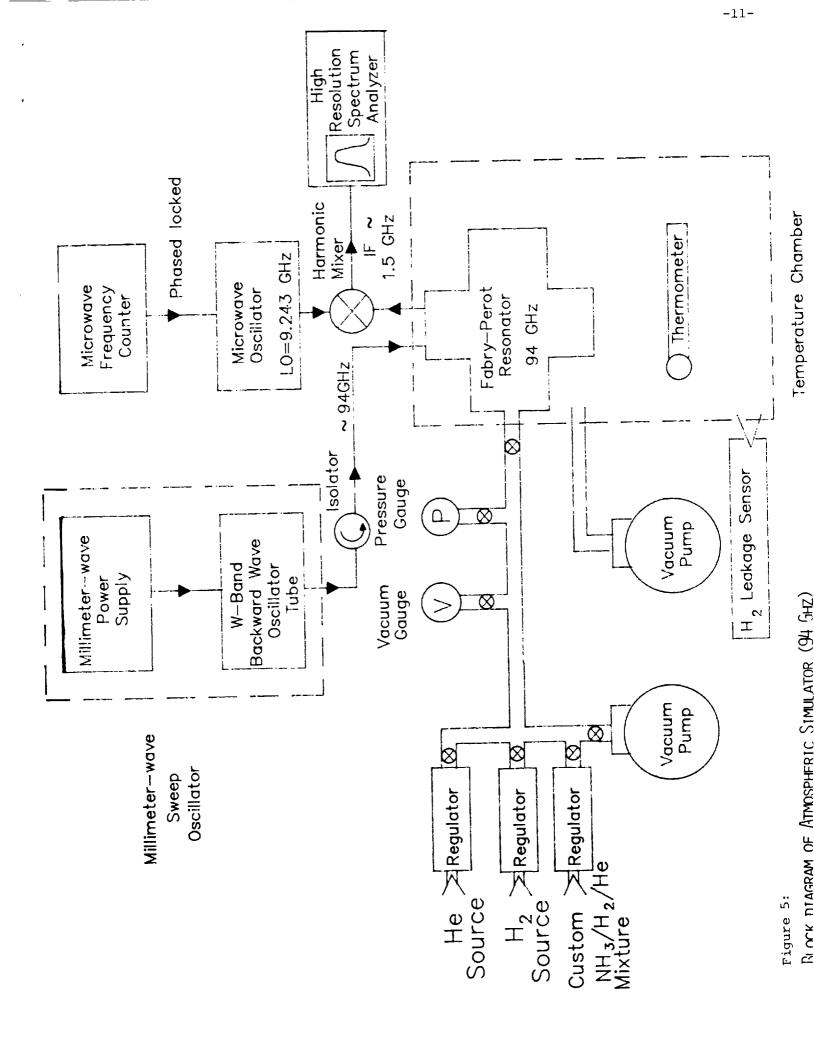
Before the absorption coefficient can be calculated, the effect of the dielectric properties of hydrogen and helium on the system must be known. The dielectric properties of gases with little or no absorption such as hydrogen and helium can cause changes in the apparent bandwidths of resonances. Because the percentage change in bandwidth (on the order of 20%) due to the absorption of NH_3 is relatively small for our system, any changes in bandwidth due to the dielectric effects of hydrogen and helium may lead to significant errors in the absorption measurement.





Dimensions of Semi-Confocal Fabry-Perot Interferometer (Resonator) used from 32-40 GHz. Figure 3:





The resonator, which operates as a bandpass filter, is connected to a signal source (the sweep oscillator) and to a receiver (the high resolution spectrum analyzer). The Q of the resonator, which is defined as the ratio of the resonant center frequency to the resonance half-power bandwidth, is proportional to the ratio of the energy stored in the resonator to the energy lost per cycle. Therefore, stronger coupling between the resonator and the spectrum analyzer or sweep oscillator causes more energy to be lost per cycle, and thus decreases the Q of the resonance. For this reason, the resonator was designed with minimal coupling, so as to maximize Q and minimize the variations in Q that might result from changes in coupling that occur when gases are introduced into the resonator. These changes in coupling, which we refer to as dielectric loading, are due to the dielectric constant or permittivity of the test gas mixtures and are not related to the absorptivity of the gases. Slight imperfections in the waveguide or irises can make the apparent Q of the resonator appear to vary with the abundance of lossless gases. It is therefore necessary to repeat the absorption measurement without the absorbing gas present. The last step in the experimental procedure is to measure the bandwidth of each resonance in a mixture consisting of 90% hydrogen (H₂) and 10% helium (He) with no ammonia present. Since, for the pressures and wavelengths involved, the H_2/He atmosphere If any apparent is essentially transparent, no absorption is expected. absorption is detected, dielectric loading (or a change in coupling due to the dielectric properties of the gases) is indicated.

We have found that the effects of dielectric loading are additive, in that they add to the apparent changes of resonator bandwidth caused by the absorbing gases. Thus, as long as the effects of dielectric loading are not time variable, they can be removed by using the measured value of the Q of the resonance with the non-absorbing gases present rather than the Q of the resonance in a vacuum for the quantity $Q_{\rm C}$ in equation (1).

C. <u>Experimental Uncertainties</u>

Uncertainties in the measurement of the absorption coefficient may be classified into two categories: uncertainties due to instrumental error and the uncertainty due to noise. The uncertainties due to instrumental error are caused by the limited resolution and capability of the equipment used to measure pressure, temperature, and resonant bandwidth. These uncertainties have been significantly reduced so that they are relatively small when compared to the uncertainty due to noise. For instance, proper calibration of the spectrum analyzer has made the uncertainty in the measurement of the resonant bandwidth and center frequency in the absence of noise negligible. Likewise, the limited ability of the temperature chamber to maintain a constant temperature results in variations of only \pm 2.5%. The largest source of uncertainty due to instrumental error in the past has been associated with the mixing ratio of the gas mixture. The uncertainty in the measurement of the amount of ammonia present in the mixture due to the inaccuracy inherent in the thermocouple vacuum gauge is on the order of $\pm 20\%$, or (1.85 \pm 0.37) % NH₃ volume mixing ratio. Thus, even though measurements at all frequencies are made with the same mixing ratio and the frequency dependence remains intact, a large uncertainty still remains in the relative amplitude of the absorption. We have been able to reduce this uncertainty by repeating the measurements using a pre-mixed, constituent analyzed, hydrogen/helium/ammonia atmosphere with a mixing ratio accuracy of better than \pm 2%, or (1.85 \pm 0.04) % NH₃ volume mixing ratio.

The most significant source of uncertainty in the measurement of the absorption coefficient is due to the effects of noise in the system. This electrical noise is displayed by the spectrum analyzer. As a result, the measurement of the bandwidth of a resonance must be accompanied by an error term which is directly related to the width of the noise on the spectrum analyzer's display.

In order to reduce the effects of noise, the system sensitivity, which is dependent on both the Q of the resonator and the noise present in the system, must be as high as possible. Because the Q is defined as 2λ times the ratio of the average energy stored in the resonator to the energy lost (per cycle) in the resonator, reducing losses in the resonator increases the sensitivity of the system. The losses in a Fabry-Perot type resonator can be attributed to the resistive losses on the surfaces of the mirrors, coupling losses due to energy coupling out of the resonator through the irises on the flat-surfaced mirror, and diffraction losses around the sides of the mirrors (Collin, 1966). (The diffraction losses are, of course, minimal in the cylindrical cavity resonators.)

Computation of the resistive losses from the mirrors of the Fabry-Perot resonators showed that, in the absence of all other losses, the quality factor should have been on the order of 250,000, whereas its actual quality factor was on the order of 10,000. Therefore, the limiting factor in the performance of the resonator must be attributed to either coupling losses or diffraction losses. (As a result, even the introduction of high temperature superconducting material would not significantly improve the sensitivity of the system.) In order to minimize the coupling losses, adjustable irises were developed so that the smallest possible coupling losses would occur, while still allowing sufficient signal coupling in and out of the resonator. However, this yielded only slightly improved results.

The major limiting factor to the system sensitivity is diffraction losses around the edges of the mirrors. One approach used to reduce diffraction losses involves the precise pointing of the mirrors to assure that both mirrors are oriented directly toward each other. This is accomplished by directing the beam of a helium-neon laser through the input waveguide and iris and into the resonator. The parabolic mirror is then adjusted so that the reflected beam focuses precisely on the output iris. This is found to maximize both the signal to noise ratio and the Q of the resonator, and therefore increase the sensitivity of the system. Figure 6 shows the improvement in the sensitivity of the 30-40 GHz system obtained with this approach. Figure 7 shows the sensitivity of the 1.34 - 23.6 GHz system shown in Figure 2.

Refractivity Measurements D.

The refractive index, n, of a gas is the ratio of the velocity of an electromagnetic wave in a vacuum, c, to the velocity of the wave in the presence of the gas, v_{g} . Since the resonant frequencies of a microwave resonator are directly proportional to the velocity of electromagnetic waves within the resonator, the refractive index of a gas can be determined by comparing the frequency of a particular resonance when a vacuum is present within the resonator, f_v , to the resonant frequency when the gas is present, f_g . That is,

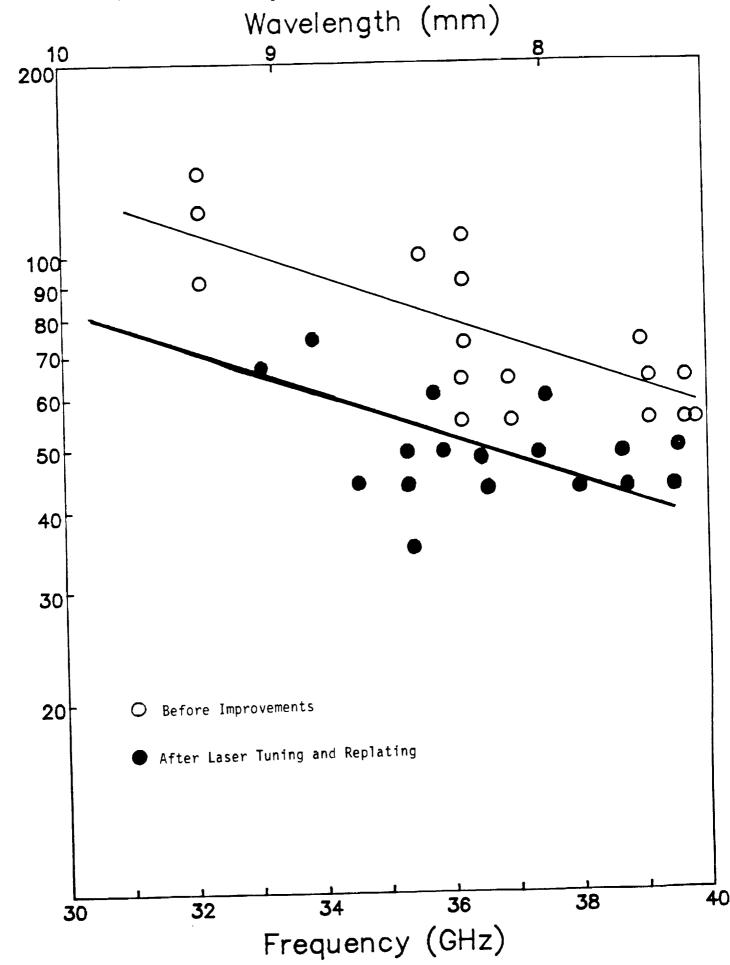
$$n = c/v_g = f_v/f_g$$
(2)

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Refractivity, N, is defined as being equal to $(n-1) \times 10^6$. Thus, it can be determined simply by measuring the change in center frequency of a given

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Figure 6: Performance (minimum detectable absorptivities) for the 32-40 GHz resonator _15system (operating at 200 K). Note improvement in average performance (solid lines) after laser tuning.



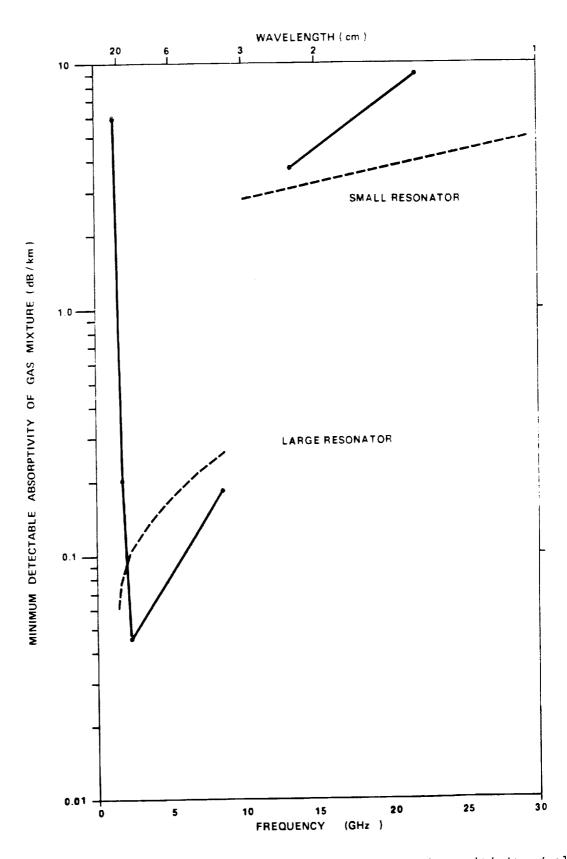


Figure 7: Predicted sensitivity (dashed line) and actual measured sensitivity (solid) of resonator system shown in Figure 2 when operated at 150 K.

resonance after the gas has been introduced. That is,

$$N = (n-1) \times 10^{6} = [(f_{v} - f_{g})/f_{g}] \times 10^{6}$$
(3)

Since the refractivity of a gas is directly proportional to the molecular density of the gas, ρ , the refractivity is often expressed in a form which is normalized by molecular density in terms of the temperature and pressure of the gas. That is, $\rho = P/RT$ where ρ is density in molecules per cm³, P is the pressure in atmosphere, R is the ideal gas constant (1.362344 x 10⁻²² cm³atm/molecule/Kelvin), and T is the temperature in Kelvins. Thus, the densitynormalized refractivity, N/ ρ , can be expressed as NRT/P. It is often assumed that the density-normalized refractivity for a gas is independent of pressure or temperature.

Any of the resonator systems described can be used to measure the densitynormalized refractivity of gas mixtures. Knowledge of this quantity is necessary determining pressure-temperature profiles from radio occultation data, and proper modeling of microwave and millimeter-wave emission. Initially, a uum is drawn in the chamber containing the resonator. The heating or cooling stem is then used to bring the chamber to the appropriate planetary perature. As the temperature is changed, the resonant frequencies change due thermal contraction. Thus, when thermal stability is reached, the resonant equencies likewise stabilize. After thermal stability is reached, a vacuum drawn in the pressure vessel containing the two microwave resonators, and the ter frequencies of the resonances of interest are than measured. A valve then opened which admits the test gas to the chamber. As the gas is added, resonances can be shifting of the center frequencies of the various erved. Once the desired pressure is reached the total frequency shift can used to compute the refractivity, N, of the gas under those conditions. It Id be noted that while the major source of uncertainty for our refractivity urements is the frequency measuring capability of our system, two other ces of uncertainty affect the accuracy of our determination of density-<u>alized</u> refractivity, and those are our abilities to measure pressure and erature.

<u>Measurements of Absorptivity and Refractivity of Solids and Liquids</u> Measurements of the absorptivity and refractivity (also referred to as the complex dielectric constants) of condensate materials have been less common at longer wavelengths because of their relatively small effect on observed microwave emission, or measured microwave absorption at the depths to which radio occultation experiments have been able to probe. However, with the upcoming Galileo mission, in which a probe carrying a microwave transmitter will penetrate into the deep Jovian atmosphere, the opportunity to measure the microwave absorption from the dense clouds may be possible. Similarly, radar studies of Titan have suggested the possibility of measuring the properties of surface liquids (Spilker and Eshleman, private communication). Therefore, in order to properly identify surface constituents based on their radar reflectivity, measurements of the complex dielectric constants of potential surface liquids are necessary at the 12.6 and 3.6 cm radar wavelengths.

Three techniques are used for the measurement of complex dielectric constants. The first is essentially identical to that previously described. That is, a system such as that shown in Figure 2 (using cylindrical resonators) is employed, and changes in the bandwidth and center frequencies of the resonances when the resonators are filled with liquid or solid materials are measured to determine refractivity and absorptivity. However, many liquids have such large amounts of refraction and absorption that the resonances are totally attenuated. With these sorts of materials, the most common alternative approach for measuring the complex dielectric constant is to place the material within an open circuited coaxial line (between the conductors), and to measure the complex impedance of the line using a microwave network analyzer. Scott and Smith (1986a) have used this technique at frequencies up to 2 GHz, and expect it to be useful to over 8 GHz. (Note that we have successfully used this technique to measure the properties of aqueous ammonia solutions up to 2 GHz.)

The third method involves placing a monopole antenna in a hemispherical tank containing the material (liquid or crystalline) to be tested. By measuring the change in the complex impedance of the antenna from when it is in air to when it is immersed in the material, it is possible to infer the complex dielectric constant of the material. Scott and Smith (1986b) have used this technique at frequencies up to 10 GHz, and expect it to be useful at much higher frequencies as long as the network analyzers to measure complex impedance are available.

Since the first two techniques described are generally not useful at wavelengths shortward of 1 cm and since the third technique has yet to be tried at millimeter-wavelengths, an alternative approach is frequently employed. Breeden and Langley (1969) developed a technique whereby a slab of solid material or a container of liquid material is placed on the surface of the flat mirror of a semi-confocal Fabry-Perot resonator, such as those shown in Figure 3 and 4. As long as the physical dimensions of the material being tested are well known, it is possible to infer its complex dielectric constant from the measured changes in the resonant frequency and quality factor of the resonator which accompany the introduction of the material. We intend to pursue this technique for future laboratory measurements of the millimeter-wave properties of potential Venus and Jovian cloud constituents.

III. CONCLUSION

In this paper, we have described techniques for laboratory measurement of microwave and millimeter-wave absorption and refraction properties of planetary atmospheric constituents. In Table I, we present a summary of known laboratory measurements of a number of planetary atmospheric constituents. It should be noted that this summary should not be considered to be complete. Similarly, even if multiple measurements are listed for a given constituent, more measurements may be necessary in order to provide a complete spectral analysis and to provide measurements over a complete range of appropriate pressures and temperatures with the necessary accuracy.

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TABLE I: REFERENCES FOR LABORATORY MEASUREMENTS OF MICROWAVE/MILLIMETER-WAVE PROPERTIES OF PLANETARY ATMOSPHERIC CONSTITUENTS

<u>CONSTITUENT</u>	REFERENCE
сн ₄	Jenkins and Steffes (1988)
CO	Britt, Tolbert, and Straiton (1961)
co ₂	Ho, Kaufman, and Thaddeus (1966) Tyler and Howard (1969)
COS	Kolbe, Buscher, and Leskovar (1977)
H ₂ 0 (g)	Ho, Kaufman and Thaddeus (1966) Jenkins and Steffes (1988) Liebe and Dillon (1969)
H ₂ O (£)	Hasted (1973)
H ₂ CO	Kolbe, Buscher, and Leskovar (1977)
H ₂ SO ₄ (g)	Steffes (1985) Steffes (1986) Fahd and Steffes (1989)
H ₂ SO ₄ (x)	Ho and Hall (in Cimino, 1982)
N ₂	Ho, Kaufman, and Thaddeus (1966)
NH ₃	Birnbaum and Maryott (1953) Bleaney and Loubser (1950) Morris and Parsons (1970) Poynter and Kakar (1975) Steffes and Jenkins (1987) Joiner, Steffes and Jenkins (1989) Spilker and Eshleman (1988)
NO	French and Arnold (1968)
0 ₂	Liebe and Layton (1969)
s0 ₂	Steffes and Eshleman (1981)
SO ₃	Steffes and Eshleman (1981)

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