

## Aircraft Observations of Venus' Near-Infrared Reflection Spectrum: Implications for Cloud Composition<sup>1</sup>

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We have obtained measurements of Venus' reflection spectrum in the 1.2 to 4.1- $\mu\text{m}$  spectral region from a NASA-Ames operated Lear jet. This was accomplished by observing both Venus and the sun with a spectrometer that contained a circular, variable interference filter, whose effective spectral resolution was 2%. The aircraft results were compared with computer generated spectra of a number of cloud candidates. The only substance which gave an acceptable match to the profile of Venus' strong 3- $\mu\text{m}$  absorption feature, was a water solution of sulfuric acid, that had a concentration of 75% or more  $\text{H}_2\text{SO}_4$  by weight. However, our spectra also show a modest decline in reflectivity from 2.3  $\mu\text{m}$  towards 1.2- $\mu\text{m}$  wavelength, which is inconsistent with the flat spectrum of sulfuric acid in this spectral region. We hypothesize that this decline is due to impurities in the sulfuric acid droplets.

We also compared our list of cloud candidates with several other observed properties of the Venus clouds. While this comparison does not provide as unique an answer as did our analysis of the 3- $\mu\text{m}$  band, we find that, in agreement with the results of Young (1973) and Sill (1973), concentrated sulfuric acid solutions are compatible with these additional observed properties of the Venus clouds. We conclude that the visible cloud layer of Venus is composed of sulfuric acid solution droplets, whose concentration is 75%  $\text{H}_2\text{SO}_4$ , or greater, by weight.

### INTRODUCTION

Venus is completely enshrouded by a cloud layer whose top is located near the 245°K temperature level of the atmosphere (Young, 1972). The atmospheric pressure at this level is about 0.1 atm (Regas *et al.*, 1973; Belton *et al.*, 1968). Speculations concerning the composition of this visible cloud layer have ranged from the obvious, such as water, to the exotic, such as hydrochloric acid, mercury, carbon suboxide, and ammonium chloride. In this paper, we present measurements of the near-infrared

reflection spectrum of Venus, and compare these measurements with theoretical calculations of the expected spectral behavior of the various cloud candidates. This comparison provides a powerful discriminant of cloud composition. In the remainder of this section, we discuss previous observations of Venus in the near-infrared portion of the spectrum, and indicate in what ways our measurements represent improvements over the earlier observations.

Just as the near-infrared portion of the spectrum contains absorption features diagnostic of particular gaseous species, so too, within this spectral region, are there bands that are characteristic of certain solids and liquids. However, aerosols are more difficult to identify than gases, because the individual rotational features

<sup>1</sup> A preliminary version of this paper, including the conclusion that the Venus clouds are composed of a water solution of sulfuric acid, was presented at the March, 1973 meeting of the Division of Planetary Sciences of the American Astronomical Society.

that are present in a gas are smeared into a single broad-absorption band in solids and liquids. Additional difficulties confront the successful application of this analytical method in the case of real planetary atmospheres. First, careful allowance must be made for the presence of gas-absorption bands. This is an important problem in the case of Venus because the major gaseous constituent, carbon dioxide, has numerous absorption bands in the near-infrared region. Second, in order to obtain the desired reflectivity spectrum, measurements must be made, not only of the planet of interest, but also, directly or indirectly, of the sun. The need for a solar comparison spectrum is dictated by the broad widths of the features of interest. Despite all these difficulties, we shall see that much compositional information can be obtained from near-infrared reflectivity observations.

Bottema *et al.* (1964, 1965) obtained reflectivity measurements of Venus from a balloon platform in the spectral region of 1.7–3.4  $\mu\text{m}$ . After allowing for the effects of gaseous absorption, they found a moderately strong absorption feature near 2  $\mu\text{m}$  and a very strong absorption feature near 3  $\mu\text{m}$ , which closely matched a water-ice cloud spectrum that was obtained in the laboratory. However, this identification has been strongly challenged: They may not have adequately corrected for the strong carbon dioxide band near 2  $\mu\text{m}$  (Rea and O'Leary, 1968). In addition, many compounds absorb near 3  $\mu\text{m}$ , where the signal-to-noise ratio of their observations is quite low.

More recently, Beer *et al.* (1971) have obtained high-resolution spectra from the ground in the 3.2–4.2- $\mu\text{m}$  region. They made a comparison observation of the sun, and because of the high resolution, they were able to make adequate allowances for absorption by telluric water vapor and carbon dioxide. These results have an adequate signal-to-noise ratio between about 3.3 and 4.0  $\mu\text{m}$ . The observed reflectivity exhibits a decline in value that starts near 3.6  $\mu\text{m}$  and progresses towards the longer wavelengths; its apparent minimum is near 3.8  $\mu\text{m}$ . Beer *et al.* suggested that these observations may

indicate that the clouds are made of bicarbonates. However, as we explain below, these absorption features are probably due to carbon dioxide.

Ground-based spectral observations of Venus in the 2.8–14- $\mu\text{m}$  region were obtained by Gillett *et al.* (1968a). Since these spectra were calibrated by referencing them to stars that were assumed to follow blackbody curves (Gillett *et al.*, 1968b), they may not be altogether suitable as reflectivity spectra. However, they appear to be in qualitative agreement with the data reported here over the limited wavelength region of possible comparison.

Finally, Kuiper and Forbes (1967) obtained measurements from the CV990 aircraft between 1.0 and 2.5  $\mu\text{m}$  with a resolution of 20  $\text{cm}^{-1}$ . While these data are valuable for analyzing gaseous absorption features in the Venus spectra, they are less useful for investigating broadband absorption. Because these spectra were obtained in daylight, they contain a large amount of scattered sunlight. Also, the comparison solar spectrum was obtained by Kuiper and Steinmetz (1967) by reflecting direct sunlight off of a block of magnesium oxide. According to Kuiper and Steinmetz, because the reflectivity of magnesium oxide gradually decreases beyond 2  $\mu\text{m}$  and because of the absence of four reflecting surfaces used in the planetary observations, the solar spectra are not strictly comparable with the planetary spectra.

The observations reported here cover the 1.2–4.1  $\mu\text{m}$  spectral region. Because they cover this range, they contain measurements both outside and within the 3- $\mu\text{m}$  cloud spectral absorption band. They therefore permit a determination of the amplitude of this feature as well as a characterization of its entire shape. None of the previous investigations cited herein contain such a complete characterization of this feature. In addition, by obtaining spectra of the sun, we could make a direct determination of the desired reflectivity spectra. Finally, our observations were taken from aircraft altitude, which permitted a view of the entire spectral region, because the water vapor content of the

residual atmosphere is several orders of magnitude smaller than at the ground. The only noticeable telluric features in our solar spectra are the 2.7- $\mu\text{m}$  bands of carbon dioxide and water vapor. Even over this narrow spectral range ( $\sim 0.1 \mu\text{m}$ ), the atmosphere is partially transparent, so that the telluric effects cancel out when the Venus spectra are ratioed with those of the sun.

### INSTRUMENTATION

The observations were made with a spectrometer that contained a circular, continuously variable interference filter as the dispersing element. The instrument package was placed at the Cassegrain focus of a 30-cm telescope mounted within a Lear jet. Below, we first describe the telescope and variable filter in greater detail, then describe other parts of the instrument, and finally discuss our wavelength calibration procedure.

The telescope used for our observations was developed by Low, Aumann, and Gillespie (1970) for use on a NASA-Ames operated Lear jet. This  $f/5.5$  telescope was mounted in a window frame of the aircraft and could view objects at elevation angles between  $19^\circ$  and  $25^\circ$ . The telescope was gyro-stabilized to about  $\pm 2$  arc min, with allowance for manual override by the observer.

The circular variable filter contains an interference coating of variable thickness along its circumference (Yen, 1969 and 1970). Each position along the wheel transmitted radiation within a 1.5% band of the central wavelength, whose value varied continuously with the position along the wheel. Because of the width of the focal plane aperture, the realized spectral resolution was about 2%. The filter consists of two  $180^\circ$  segments, bonded together. One segment permitted spectral scans from about 1.2–2.35  $\mu\text{m}$ , and the second segment covered the spectral range from about 2.25–4.45  $\mu\text{m}$ . However, the detector response limited the useful spectral range to values less than about 4.1  $\mu\text{m}$ .

The instrument is shown schematically in Fig. 1. The filter wheel rotated con-

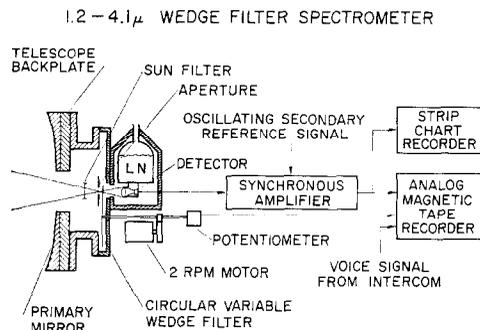


FIG. 1. Schematic layout of the instrument.

tinuously at two revolutions per minute. Light that passed through the aperture and the filter entered the evacuated dewar through a sapphire window and was then reimaged by a 9-mm sapphire lens onto a  $2 \times 2$ -mm PbS detector that was cooled to about  $77^\circ\text{K}$ . The intensity could be reduced by a factor of about  $10^6$  for solar observations by inserting a thin sheet of brass with four 0.025 mm-diameter holes placed 5 cm ahead of the focal plane. Modulation of the signal and subtraction of sky background were achieved by oscillating the secondary mirror of the telescope at 26 Hz. In each of the two resulting beams (corresponding to the two extreme positions of the secondary mirror) the field of view was 6 arc min. The beam separation was 12 arc min between centers.

The signal from the PbS detector traveled through a low-noise cable to a phase-lock amplifier that was referenced to the oscillating secondary mirror drive. The signal was amplified and recorded on one channel of an analog magnetic tape unit. Information on the angular position of the circular filter was obtained by recording, on a second channel, the voltage from a potentiometer that was coupled to the drive shaft of the filter. A third channel was used to record comments of the operator, who noted values of the instrument settings and other circumstances of the observations.

Calibration of the wavelength scale in terms of the recorded potentiometer voltage was accomplished as follows: Voltages that corresponded to several wavelengths were established by observing

narrow lines from a Xenon calibration lamp. To within 5% the potentiometer voltage was a linear function of the angular position of the wheel. The manufacturer of the wheel supplied data that related orientation angle and wavelength; these data were used to interpolate between the laboratory calibration points. Verification of the wavelength scale was made by measuring the positions of telluric and Cytherian carbon dioxide and water-vapor bands that are present in the spectra of Venus and the sun. We used spectra that were obtained from both the Lear jet and the ground for this purpose. This determination indicated that the overall uncertainty in our wavelength scale is only  $\pm 0.005 \mu\text{m}$ . The term wavelength scale refers to the relationship between directly measured potentiometer voltage and wavelength and should not be confused with our spectral resolution, which as mentioned elsewhere in this paper is about 2%.

#### OBSERVATIONS

In this section we describe our experimental procedure and data reduction, discuss briefly our solar comparison observations, and finally present our measurements of Venus' reflection spectrum. Two sets of observations were carried out: During the week of July 16, 1972, we obtained spectra of Venus and the sun from the Lear jet, and during the spring of 1973, we obtained ground-based spectra of the sun and the moon. The latter set of data will be dealt with later in this section, when we discuss our solar spectra. The aircraft observations were made when Venus was rising with an angular separation from the sun of about  $40^\circ$ . The phase angle was approximately  $120^\circ$ . All of our observations of Venus were made before the sun was above the horizon, because previous observations from the ground indicated that after the sun had risen, a serious scattered-sunlight problem was present in the data. Solar comparison spectra were obtained about two hours after the Venus data. Because the atmos-

pheric transmission is close to 100% throughout virtually our entire spectral region, it was not necessary to obtain the solar spectra at precisely the same moment as our Venus spectra.

Typically, about five spectral scans were taken with the object in one of the two image fields defined by the oscillating secondary, followed by five scans with the object in the other beam. This procedure was repeated a number of times during a given flight, resulting in a "left beam" series and "right beam" series of observations. Measurements of a given object lasted about 30 min.

The analog record of the data was edited during digitization to eliminate portions that were taken while the telescope was not tracking the object in either beam, as occurred when the beam was being switched or when there was improper guiding. A strip-chart record, also obtained during the observations, served as a guide for performing the editing. Digitization of the detector signal and potentiometer voltage was made at a rate of 150 samples per scan.

The digitized data were then processed through a computer to permit co-adding of the individual spectra and determination of the wavelength scale. To a first approximation, sky noise was removed by chopping one beam against the second beam. However, some residual sky contribution remained because of small asymmetries in the angular extent and the viewing angles between the two beams. By appropriately adding spectra that were obtained with the object first in one beam and then in the second beam, we obtained a second-order removal of the sky noise. By appropriately subtracting these two sets of data, we eliminated the signal and obtained an estimate of the sky noise. The above second-order correction for sky noise proved to be valuable for the Venus spectra, but unnecessary for the substantially stronger solar signals. The determination of the residual sky noise provided a useful means of determining the overall signal-to-noise ratios of the observations, since in practice the sky spectra contained a contribution from a

number of noise sources, including detector and guiding error.

While, as expected, individual solar spectra had high signal-to-noise values, they presented us with two problems. First, examination of the four-hole sun filter—after the flight series—showed that one hole was larger than the other three holes. As a result, it was possible that our solar spectra contained a systematic wavelength bias due to diffraction effects. Second, examination of the solar spectra showed that the signal strength at the longest wavelengths increased with time. This latter problem was believed to be due to the sun's heating parts of the telescope, resulting in a source of thermal emission that increased in strength with time. To evaluate these two problems, we obtained ground-based observations of the sun and moon. The solar spectra were obtained by using the four-hole filter, a nine-hole filter that had holes of the same diameter, and a cover that contained larger holes. The cover was placed over the telescope aperture.

Fortunately, with the aid of the ground-based observations, we were able to resolve satisfactorily both problems. First, lunar reflectivity values determined at the shorter wavelengths from lunar observations without a filter and from solar observations with the four-hole filter were in good accord with the results of McCord and Johnson (1970). This indicated a lack of any significant diffraction effect. Second, the ground-based solar spectra that were obtained with the hole-containing cover over the front aperture showed no growth of signal at the longer wavelengths. A comparison of these cover spectra with the first sun spectrum that was obtained from the Lear jet showed good agreement, indicating an absence of significant thermal emission in this initial spectrum. Accordingly, we used this first Lear-jet sun spectrum in determining Venus' reflectivity.

Figure 2 shows two separate determinations of the reflectivity spectrum of Venus. Each determination represents the sum of three sets of right- and left-beam spectra of Venus, i.e., altogether about 30 individual spectra. In both cases, the co-added

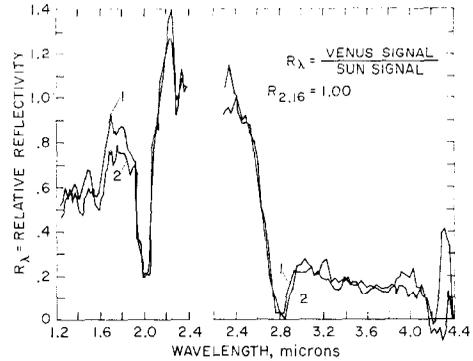


FIG. 2. Reflectivity of Venus as a function of wavelength. The reflectivity values are on a relative scale, which has been normalized to have a value of 1 at 2.16  $\mu\text{m}$ . The two curves represent two separate sets of data. Each set contains 30 separate spectra of Venus.

Venus observations were divided by the first solar spectrum. The spectra are divided into two parts, corresponding to the two halves of the filter wheel. All these data are from observations which were made on the morning of July 21.

The reflection spectra are on a *relative* scale, i.e., they represent the variation of reflectivity with wavelength. No attempt has been made to determine the absolute value of the reflectivity at a given wavelength. The spectra have been normalized to have a value of 1 at a wavelength of 2.16  $\mu\text{m}$ .

We see that the two spectra are in good agreement. The absorption features located near 1.4, 1.6, 2.0, and 2.8  $\mu\text{m}$  are due to carbon dioxide absorption in the atmosphere of Venus. The small-scale variations in the spectra are most likely caused by noise that is due primarily to the limited guiding capability of the telescope. The very strong absorption band between 3 and 4  $\mu\text{m}$  is caused principally by cloud-aerosol absorption and is the subject of the analysis presented in the next section. As individual right- and left-beam series show a greater dispersion for the second set of data in Fig. 2 than for the first, we will use the first set for comparison with our theoretical spectra.

A potentially serious problem arises when we compare our relative reflectivity curve in the 1.25–2.5- $\mu\text{m}$  region with the

albedo results of Irvine *et al.* (1968). Irvine *et al.* made very accurate, narrow band photoelectric observations of Venus and found that its bond albedo was 0.89 at 1.06  $\mu\text{m}$ . Chiefly due to the uncertainty in the  $V$  magnitude of the sun, their uncertainty in this value is on the order of 10%. It might appear from Fig. 2 that the above albedo value would imply an albedo considerably in excess of 1 near 2  $\mu\text{m}$  which of course is physically impossible.

However, we do not believe our results are necessarily in conflict with Irvine *et al.*'s 1.06  $\mu\text{m}$  albedo. First it must be pointed out, as we have above, that small scale variations in albedo, such as the spike near 2.2  $\mu\text{m}$ , must be viewed with skepticism, because of telescope guiding problems and other noise sources. Thus one must average our results over small wavelength intervals before making use of them. Within this framework, curve 1 of Fig. 2 implies that the ratio of Venus' reflectivity near 1.3  $\mu\text{m}$  to that near 2.1  $\mu\text{m}$  is  $0.65 \pm 0.2$ , where the error bars reflect our overall uncertainty in this ratio. Furthermore given the possibility that Venus' reflectivity may decline between 1.06–1.3  $\mu\text{m}$  we see that the observed modest decline in reflectivity between 2.1–1.3  $\mu\text{m}$  is not necessarily in conflict with Irvine *et al.*'s albedo value at 1.06  $\mu\text{m}$ .

While the exact value of this decline is not well established from our results reported here, we feel quite confident of its reality for two reasons: First, as mentioned above, we were able to derive a relative reflectivity curve for the moon in this same wavelength region that agreed quite well with the results of others. Second, data taken since the observations reported here, also show a modest decline in Venus' reflectivity from 2.1–1.3  $\mu\text{m}$ . These latter observations included measurements of the sun taken with a more appropriate sun screen.

Figure 3 shows the sky spectrum obtained for the first data set. It has been drawn to the same scale as the results in Fig. 2 so that the ratio of the absolute value of the vertical displacement of a

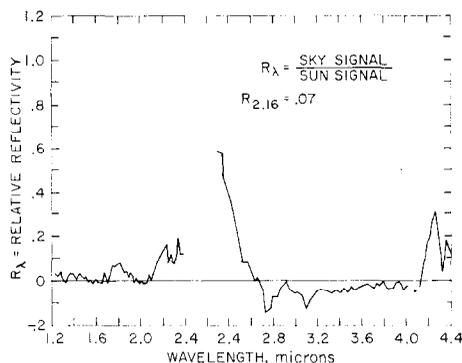


FIG. 3. Sky noise as a function of wavelength for the first data set of Fig. 2. The scale is the same as that of Fig. 2.

point in Fig. 2 to that of a point at the same wavelength in Fig. 3 gives a measure of the signal-to-noise ratio. We see that the signal-to-noise ratio substantially exceeds unity at all wavelengths below about 4.1  $\mu\text{m}$ , including the region of the 3- $\mu\text{m}$  band. The poor signal-to-noise ratio at wavelengths above 4.1  $\mu\text{m}$  is caused primarily by a sharply diminishing detector responsivity.

#### COMPARISON WITH CLOUD CANDIDATES

We now compare the reflectivity properties of the various cloud candidates with our observations of Venus' reflectivity spectrum. The theoretical reflectivity spectra were derived by using a Mie scattering computer program to specify the single scattering properties of the cloud aerosols and by using a second computer program, based on Hansen's (1969) doubling method, to solve the multiple scattering problem. The results of the doubling calculation were integrated over the illuminated disk of Venus for the phase angle of observation.

In order to carry out these calculations for a given candidate, we must first specify several properties of both it and the clouds. These include the optical constants of the material at all wavelengths of interest, the particle-size distribution function and the optical depth of the clouds at some reference wavelength. The sources

of the optical constants are given in Table I. We adopted the size distribution function inferred by Hansen and Arking (1971) from the polarization characteristics of the Venus clouds. Our calculated spectra depend principally on the value of the

cross-section-weighted average of the particle size and are fairly insensitive to other characteristics of the distribution function (Hansen and Pollack, 1970). Hansen and Arking (1971) obtained a value of  $1 \mu\text{m}$  for the average particle radius. The effect

TABLE I  
SOURCES OF OPTICAL CONSTANTS

Substance	Source	Comments
Mercury	Hodgson (1959)	Hodgson provides measurements of $n_r^a$ and $n_i^a$ from 1.2 to 2.5 $\mu\text{m}$ . Using equations given by Van de Hulst (1957) for metals, we extrapolate these values to longer wavelengths.
Ammonium chloride	Hodgman (1956), Robertson and Williams (1973)	Hodgman gives a value for $n_r$ at visual wavelengths. The 3 $\mu\text{m}$ band is sufficiently weak so that $n_r$ should be fairly constant with wavelength. Robertson and Williams give values of $n_i$ for liquid ammonia. Values of $n_i$ for ammonium chloride were derived from these data by assuming $n_i$ scales as the volume density of $\text{NH}_3$ molecules. We also shifted the wavelength scale slightly so that the band centers coincided with the observed positions.
Hydrated ferric chloride ( $\text{FeCl}_2 \cdot 2 \text{H}_2\text{O}$ )	Kuiper (1969), Pollack <i>et al.</i> (1973)	Kuiper gives a value for $n_r$ at visual wavelengths. We assumed $n_r$ was a constant over our wavelength range for the same reason as in the case of ammonium chloride. Pollack <i>et al.</i> (1973) give values for $n_i$ for hydrated water. Values of $n_i$ for $\text{FeCl}_2 \cdot 2 \text{H}_2\text{O}$ were derived from these using the same method as for ammonium chloride. No allowance was made for absorption due to Fe ions at wavelengths below 2 $\mu\text{m}$ .
Liquid water	Irvine and Pollack (1968)	
Water ice	Irvine and Pollack (1968), Hansen and Pollack (1970)	Irvine and Pollack's optical constants were modified in the 3 $\mu\text{m}$ region according to the prescription given by Hansen and Pollack.
Hydrochloric acid	Williams (1973), Hapke (1973)	Value of $n_i$ between 2.5–4.0 $\mu\text{m}$ and values of $n_r$ over the whole wavelength region were obtained from Williams. Williams derived these by applying the Kramers–Kronig relations to his reflectivity measurements. We derived $n_i$ values below 2.5 $\mu\text{m}$ from transmission measurements made by Hapke. We did this by using Beer's law.
Sulfuric acid	Palmer and Williams (1973), Neumann (1973)	Making use of reflection measurements by Palmer and Williams, we applied the Kramers–Kronig relationships to derive $n_r$ values from 1.2–4.0 $\mu\text{m}$ and $n_i$ values from 2.5–4.0 $\mu\text{m}$ . Neumann gives values of $n_i$ below 2.5 $\mu\text{m}$ .

<sup>a</sup>  $n_r$  and  $n_i$  are the real and imaginary index of refraction, respectively.

of other choices of mean size will be discussed near the end of this section. Hansen and Arking also found that the particles are spherical; thus, our calculations, which are based in part on the use of Mie theory, contain no compromising numerical approximations.

We choose a value of 32 for the optical depth of the clouds at visual wavelengths, based upon an analysis of the observed reflectivity of the clouds by Sagan and Pollack (1967). This value is not very well-determined, although we know the optical depth is large. Fortunately, our results are very insensitive to the exact value of the optical depth. For example, changing the value of the optical depth by a factor of two in either direction only changed the shape of the reflectivity spectrum by a few percent.

Before proceeding to the comparison between the observed and predicted spectra, we need to assess the influence of absorption caused by carbon dioxide upon our observed spectrum. In this way we can determine the extent to which the cloud aerosols are responsible for the observed absorption at a given wavelength. As we remarked above, carbon dioxide is chiefly responsible for the strong, narrow absorption features located near 1.4, 1.6, 2.0, and 2.8  $\mu\text{m}$  in our Venus spectrum. In addition, as shown below, the short wavelength tail of the 4.3- $\mu\text{m}$  carbon dioxide fundamental may contribute significant absorption above 3.6  $\mu\text{m}$ .

We made an estimate of the absorption that is due to carbon dioxide by averaging laboratory data obtained in the 2.5–4.5- $\mu\text{m}$  region over the resolution of our spectrometer. There was less of a need to do this at shorter wavelengths, where the bands of carbon dioxide are weaker and generally confined to well-known wavelength boundaries. For the purpose of this calculation, we assumed that the carbon dioxide absorption could be modelled by a simple reflecting layer model; while multiple scattering within the clouds appears to play a dominant role in line formation (see e.g., Belton *et al.*, 1968; Regas *et al.*, 1973), a simple reflecting layer model should be a useful approxima-

tion for our interests (Pollack and Sagan, 1968).

Our objectives in estimating the amount of carbon dioxide absorption in the 2.5–4- $\mu\text{m}$  region are twofold: to determine which regions are almost entirely free of carbon dioxide absorption, and to make a crude estimate of the amount of carbon dioxide absorption in regions where there is a moderate amount of gaseous opacity. Accordingly, we will use laboratory spectra obtained at a somewhat different temperature from that at the cloud tops and we will use a simple scaling relationship between pressure and gas amount. Also we will do the calculations for two sets of gas amounts and pressures that bracket the most likely values.

All the carbon dioxide bands of interest lie on the strong-line portion of the curve of growth, for which the absorption is a function only of the product of gas pressure and gas amount,  $PW$ . A similar dependence is exhibited by the wing of the 4.3- $\mu\text{m}$  band (Burch *et al.*, 1968a). Making use of the extensive analysis of Young (1972) for a wide variety of carbon dioxide bands and interpreting her results within the context of a simple reflecting layer model, we find that in the near infrared the product  $PW$  for Venus is typically 0.3 km atm<sup>2</sup>. The above product includes an allowance for the two-way transmission of radiation through the Venus atmosphere at a variety of slant paths. The value of  $PW$  for a given band of carbon dioxide within the list considered by Young may differ by up to a factor of 5 from the average quoted above, with regions of weaker gaseous absorption being characterized by larger products in general.

Figure 4 shows the transmission spectra of carbon dioxide for several values of  $PW$ , which lie on either side of the  $PW$ -value estimated above from Young's results. These spectra were derived from the laboratory data of Burch *et al.* (1968b) and Gryvnak *et al.* (1966) and, as mentioned above, were averaged over the effective resolution of our spectrometer. From the difference between the carbon dioxide transmission values and our observed spectrum of Venus, we see that strong

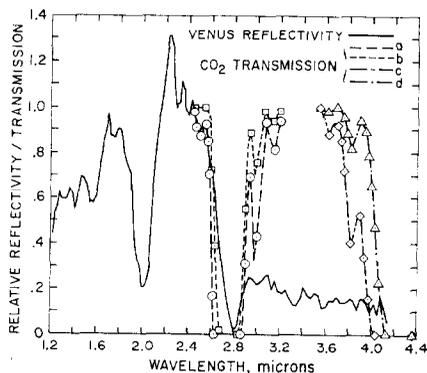


FIG. 4. Transmission of carbon dioxide as a function of wavelength for several values of the product  $PW$ . (a)  $PW = 1.38 \text{ km atm}^2$ . (b)  $PW = 0.130 \text{ km atm}^2$ . (c)  $PW = 0.82 \text{ km atm}^2$ . (d)  $PW = 0.065 \text{ km atm}^2$ . Also shown is the reflectivity of Venus, as given by the first data set of Fig. 2.

aerosol absorption is present for Venus in the entire 3–4- $\mu\text{m}$  region. From wavelengths of 3.05–3.6  $\mu\text{m}$ , the observed spectrum is quite close to that of the clouds only. From 3.6  $\mu\text{m}$  out towards 4.3  $\mu\text{m}$ , carbon dioxide contributes an increasing amount of absorption. Except for the feature near 3.8  $\mu\text{m}$ , this gaseous absorption arises from the tail of the 4.3  $\mu\text{m}$  fundamental. Between 2.95  $\mu\text{m}$  and 3.05  $\mu\text{m}$ , carbon dioxide contributes a non negligible amount of absorption to the observed spectra.

The failure of the laboratory transmission curves to follow the observed curve near the center of the 2.75- $\mu\text{m}$  carbon dioxide band is an indication of the limitations of the simple reflecting layer model. Near the 2.75  $\mu\text{m}$  band center, the observed reflectivity is systematically higher than the transmission curves of the laboratory data. This difference may be an indication of the presence of aerosols at very high altitudes in the Venus atmosphere.

The observed position of the minimum of the 2.75- $\mu\text{m}$  carbon dioxide bands is shifted by about 0.05  $\mu\text{m}$  above its expected position. As mentioned above, the uncertainty in our wavelength calibration is smaller than this shift, so we believe this may be a real effect. The shift may be an indication that the reflectivity of the

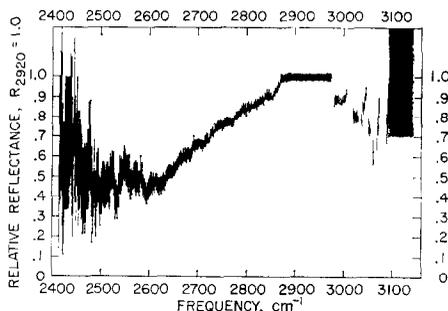


FIG. 5. Reflectivity of Venus as measured by Beer *et al.* (1971).

clouds is rapidly declining over this wavelength interval. Alternatively, we may have underestimated the uncertainty in our wavelength scale.

We now discuss in greater detail the carbon dioxide absorption at wavelengths above 3.6  $\mu\text{m}$  by comparing the laboratory gas-absorption data with the Beer *et al.* (1971) observations. Figure 5 shows the Beer *et al.* reflectivity results, which were discussed in the Introduction. These observers proposed that the decline in reflectivity towards lower wave numbers (higher wavelengths), with an apparent minimum near 2600  $\text{cm}^{-1}$  (3.8  $\mu\text{m}$ ), was produced by the cloud aerosols, and suggested as a result that the cloud particles might be bicarbonates. Comparing Figs. 4 and 5, we see that the observed spectral feature might be due to absorption by carbon dioxide. This point is illustrated in greater detail in Fig. 6, which shows the original, high-resolution laboratory spectra for a  $PW$  product of

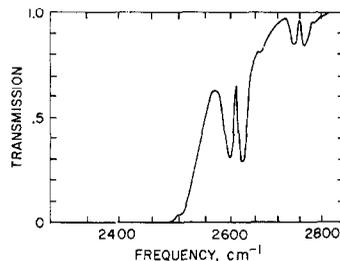


FIG. 6. Transmission of carbon dioxide as a function of wavenumber from the laboratory spectra of Burch *et al.* (1968a). Here  $PW = 0.8 \text{ km atm}^2$ , a value close to that of the top portion of the Venus atmosphere.

0.8 km atm<sup>2</sup>. The laboratory spectrum was obtained at room temperature; however, we do not expect the spectrum to undergo a substantial modification between room temperature and the temperature near the tops of the Venus clouds. The spectral feature, which appears in the laboratory spectra close to the position of the feature in Beer's observations, is due to the  $00^{\circ}0 \rightarrow 12^{\circ}0$  vibration band of the carbon dioxide isotope  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ . The rather close correspondence of the laboratory data with Beer's results suggests that the reflectivity decrease beyond  $3.6 \mu\text{m}$  is chiefly the result of absorption by carbon dioxide. To a first approximation, the reflectivity of the clouds would appear to be relatively constant over the spectral region from  $3.6$ – $4.0 \mu\text{m}$ .

The above discussion of the role of carbon dioxide absorption near  $4.0 \mu\text{m}$  is meant only as a commentary on the interpretation by Beer *et al.* of their very fine spectrum of Venus and not as a criticism of their excellent data.

Our spectra are in rough agreement with the trends indicated in Beer *et al.*'s spectra. Averaging over small wavelength intervals so as to eliminate the "high frequency" noise in our data, we find that between wavelengths of  $3.0$ – $3.2 \mu\text{m}$ , the average relative reflectivity of Venus is about 0.22, while between  $3.8$ – $4.0 \mu\text{m}$  it is about 0.13. Thus our data also show a lower reflectivity near  $4 \mu\text{m}$  than that near  $3 \mu\text{m}$ .

The above discussion of Figs. 4, 5, and 6 also indicates that over a significant portion of the  $2.5$ – $4.0$ - $\mu\text{m}$  region, the *PW* product that characterizes the carbon dioxide absorption is similar to the values that are found at shorter wavelengths. The significance of this conclusion is discussed in the next section.

We are now prepared to make a comparison between our observations of Venus' reflectivity and that predicted by a number of proposed cloud candidates. We will direct our attention particularly to matching the  $3$ - $\mu\text{m}$  absorption feature, which, in the observed spectrum, is the strongest band that can be attributed to the cloud aerosols. In order for a successful match

to occur, the predicted and observed spectra should be quite close between about  $3.05$ – $3.6 \mu\text{m}$ , while the predicted reflectivity should lie above the observed values by increasing amounts as the wavelength increases beyond  $3.6 \mu\text{m}$ . Factor-of-2 differences are considered acceptable at  $3.9$  microns. In the  $2.95$ – $3.05$ - $\mu\text{m}$  region the predicted curve can be as much as a factor of two larger than the observed reflectivity. Of course, it should not be significantly less than the observed value in any spectral region.

Figures 7 through 11 show a comparison between the spectral properties of a number of proposed cloud constituents and our Venus observations. Each graph contains the curve of the first data set of our July 21 observations. All theoretical curves have been normalized to have the same reflectivity as the observed value at  $2.16 \mu\text{m}$ . At this wavelength, the observed reflectivity has a value close to our average observed value in the  $2.1$ – $2.4$ - $\mu\text{m}$  region, which lies near the short wavelength boundary of the  $3$ - $\mu\text{m}$  absorption band. As stated above, the reflectivity values are on a relative scale, which arbitrarily has a value of 1 at  $2.16 \mu\text{m}$ . Except for one of the mercury curves in Fig. 7 and the HCl curves in Fig. 11, all the calculations were performed by using

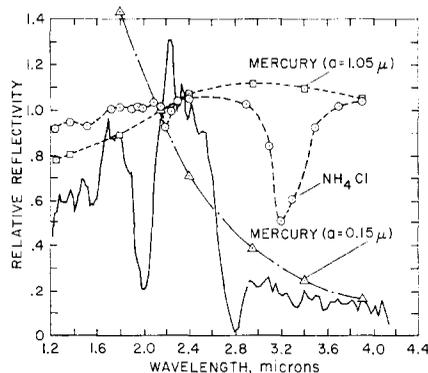


FIG. 7. A comparison of the predicted reflectivity behavior of liquid mercury and ammonium chloride with that of the Venus observations reported in this paper. The lower mercury curve represents the results for a mean particle size of  $0.15 \mu\text{m}$ . The remaining curves were for particle size of  $1 \mu\text{m}$ .

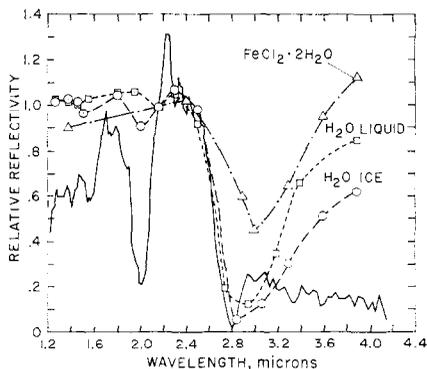


FIG. 8. A comparison of the predicted reflectivity of hydrated iron chloride, liquid water and water ice with the observed Venus reflectivity. All the theoretical curves were computed for a particle size of  $1 \mu\text{m}$ .

a mean particle size of  $1 \mu\text{m}$ . We first discuss the calculations of clouds containing  $1\text{-}\mu\text{m}$  particles.

We see that most materials show very little similarity with the observed reflectivity curve of Venus in the  $3\text{-}4\text{-}\mu\text{m}$  region; materials in this category include a number of compounds, such as water and ammonium chloride, which have a strong  $3\text{-}\mu\text{m}$  spectral feature.

Acid clouds, as represented by the calculations for HCl and  $\text{H}_2\text{SO}_4$  solutions in Figs. 9 and 10 come closest to matching the observations. Because these compounds are binary mixtures of water and a second

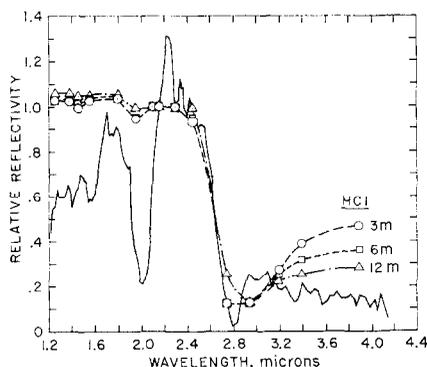


FIG. 9. A comparison of the predicted reflectivity of HCl solutions of several concentrations with the observed Venus reflectivity. All the theoretical curves were computed for a particle size of  $1 \mu\text{m}$ .

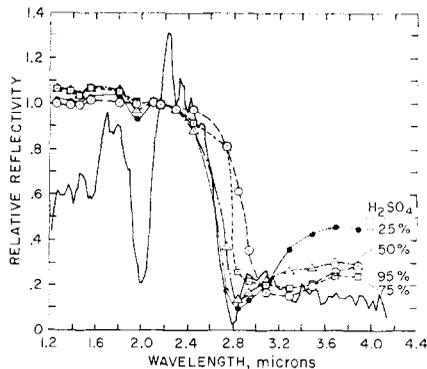


FIG. 10. A comparison of the predicted reflectivity of  $\text{H}_2\text{SO}_4$  solutions of several concentrations with the observed Venus reflectivity. All the theoretical curves were computed for a particle size of  $1 \mu\text{m}$ .

material, the calculations were carried out for several concentrations of these solutions. While the reflectivity behavior of the HCl solutions comes closer to matching the observations than many other materials, it still is in conflict with the observations: The curves of the HCl solutions exhibit too low a reflectivity near  $3.0 \mu\text{m}$ , and then rise noticeably in reflectivity from  $3.0 \mu\text{m}$  towards longer wavelengths. The  $6\text{-M}$  HCl solution is close in value to the concentration of the HCl cloud that was proposed by Lewis (1972a) on the basis of the observed partial pressure of HCl and  $\text{H}_2\text{O}$  vapor.

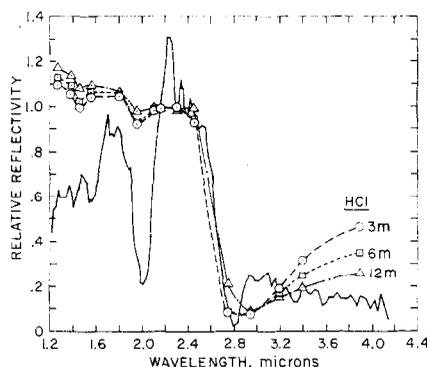


FIG. 11. A comparison of the predicted reflectivity of HCl solutions of several concentrations with the observed Venus reflectivity. In this case, the theoretical curves were computed for a mean particle size of  $2 \mu\text{m}$ .

The reflectivity curves of the  $\text{H}_2\text{SO}_4$  solutions show a systematic variation with concentration. As the concentration increases, the center of the band shifts to longer wavelengths, and broadens. The lower concentration solutions, the 25% and 50% solutions of  $\text{H}_2\text{SO}_4$  by weight, have reflectivity curves that disagree with the observations in a manner similar to the HCl solutions. Both the higher concentration solutions (75% and 95%) have curves which are consistent with the observations. Unfortunately, their reflectivity values differ significantly from one another in the 2.95–3.04- $\mu\text{m}$  region, where the carbon dioxide absorption is uncertain and could be significant. It is interesting to note that for both concentrations, but particularly for the 75% solution, the reflectivity values change significantly near the center of the 2.75- $\mu\text{m}$  carbon dioxide band and could account for the shift in the observed minimum in this spectral region. Thus, of all the materials investigated, only the highly concentrated solutions of  $\text{H}_2\text{SO}_4$  ( $\geq 75\%$   $\text{H}_2\text{SO}_4$  by weight) match our observations of Venus in the 3- $\mu\text{m}$  region.

In general, agreement with the observations cannot be achieved simply by choosing a different value for the mean particle size. This point is illustrated in Fig. 7 for mercury clouds and in Fig. 11 for HCl clouds. Mercury behaves optically like a metal in the near infrared. As long as  $x$ , the ratio of the circumference of a mercury aerosol to the wavelength, is greater than unity, the mercury aerosol behaves like a nearly perfect reflector. However, as  $x$  drops below unity it starts becoming a good absorber. Thus one might speculate that the 3- $\mu\text{m}$  band could be generated simply by picking a mean particle size so that  $x$  falls below 1 above 3  $\mu\text{m}$ . Calculations for 0.15  $\mu\text{m}$  mercury particles are shown in Fig. 7 to explore this possibility. While a low reflectivity is achieved in the 3–4- $\mu\text{m}$  region, the calculated curve does not provide a good match with the observations: The predicted reflectivity rises too slowly towards wavelengths shortward of 3  $\mu\text{m}$ . A similar result would be found if we used smaller

particle sizes for some of the other candidates.

Figure 11 illustrates the effects achieved by increasing the mean particle size of the HCl solution aerosols from 1 to 2  $\mu\text{m}$ . While agreement can be obtained at a particular wavelength, the overall shape of the calculated spectra remains in conflict with the observed behavior: The reflectivity is too low near a wavelength of 3.0  $\mu\text{m}$  and too high above 3.4  $\mu\text{m}$ .

In addition to the materials shown in Figs. 7–11, a number of other materials were considered. In all cases, however, their spectra proved to be incompatible with our observations. Optical constants were available for some of these materials, but their imaginary indices of refraction were so small that their reflectivity curves had a constant value, and so are not shown in this article. Examples in this category are bicarbonates, whose laboratory spectra, however, do show an absorption band present near 4  $\mu\text{m}$ . The laboratory studies show a band while our calculations do not, because the laboratory results deal with powders that have particle sizes that are orders of magnitude larger than the polarimetric value for the Venus clouds. In other cases considered, optical constants were not available, but existing laboratory spectra showed little resemblance to our Venus observations. Table II summarizes the additional materials considered and the source of their infrared spectra.

Thus we have seen that only sulfuric acid solutions, with concentrations of 75% or more, are consistent with our observations in the 3- $\mu\text{m}$  region. Because all of the rejected materials that were considered have reflectivity values above the observed spectra in the 3.2–3.6- $\mu\text{m}$  region, mixtures of rejected materials are also inconsistent with the observations.

So far, we have focused our attention on trying to match the strong 3- $\mu\text{m}$  band. Our observations suggest that the reflectivity declines somewhat from 2  $\mu\text{m}$  to 1  $\mu\text{m}$ . The  $\text{H}_2\text{SO}_4$  curves of Fig. 10 display no significant variation in this wavelength interval. As discussed in the next section, we postulate that the  $\text{H}_2\text{SO}_4$  clouds contain impurities, such as dissolved iron,

TABLE II  
OTHER MATERIALS EXAMINED

Substance	Source	Comments
Mercuric chloride ( $\text{Hg}_2\text{Cl}_2$ )	Fink and Burke (1971)	Fink and Burke's reflectivity spectra of powdered $\text{Hg}_2\text{Cl}_2$ shows no large absorption feature in the $3\ \mu\text{m}$ region. The mean particle size was between $25\text{--}50\ \mu\text{m}$ .
Nitric acid	Marcus and Fresco (1957)	Marcus and Fresco give transmission spectra for several concentrations. The cell thickness was about $2\ \mu\text{m}$ . The spectra show a band center near $3.0\ \mu\text{m}$ with $n_i$ rapidly decreasing from $3.0\text{--}4.0\ \mu\text{m}$ . A cloud made of this material would behave similarly to our computed spectra for water ice.
Carbon suboxide	Smith <i>et al.</i> (1963), and Plummer and Carson (1970)	Carbon suboxide monomer has a feature centred at $2.27\ \mu\text{m}$ , which is not present in either our or Kuiper and Forbes (1967) spectra. Even though it has a strong band near $3\ \mu\text{m}$ , the reflectivity of the band increases significantly at wavelengths above $3.3\ \mu\text{m}$ . Hydrated carbon suboxide polymer has only a very weak feature in the $3\ \mu\text{m}$ region.
Hydrocarbons	Plummer (1969)	Hydrocarbons show a feature near $2.4\ \mu\text{m}$ which is not present in either our spectra or that of Kuiper and Forbes (1967). Since the dipole moment of CH is significantly less than that of NH, we suspect that a cloud made of this material would have an even weaker $3\ \mu\text{m}$ band than that shown by $\text{NH}_4\text{Cl}$ .
Sundry hydrated silicates	Pollack <i>et al.</i> (1973)	These would have a lower volume density of $\text{H}_2\text{O}$ molecules than $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ , and therefore a weaker $3\ \mu\text{m}$ band.
Bicarbonates and carbonates	Grey (1963)	The $n_i$ value of $\text{CaCO}_3$ and, by implication, that of other carbonates and bicarbonates is very small. Therefore, clouds consisting of $1\ \mu\text{m}$ -sized particles of this material would show no appreciable absorption in the $3\ \mu\text{m}$ spectral region.
Ammonium sulfate	Fink and Burke (1971)	The reflection spectrum of powdered ammonium sulfate is similar to that of ammonium chloride.

which are responsible for this spectral feature. A similar suggestion has been made by Hapke (1972) to explain the low reflectivity of the Venus clouds in the ultra-violet region. Hapke made this suggestion at a time when it appeared that the clouds were composed of HCl solution. However, he has pointed out that the same arguments apply for  $\text{H}_2\text{SO}_4$  clouds (Hapke, 1973).

## DISCUSSION

We first consider the compatibility of the proposed cloud constituents with other observed properties of the clouds. This discussion provides additional evidence in favor of sulfuric acid clouds. Later in this section, we consider some of the implications for Venus of the presence of sulfuric acid clouds.

Besides matching our near-infrared spectra, any cloud candidate must also pass several other tests. From an analysis of the polarization behavior of the Venus clouds, Hansen and Arking (1971) and Hansen (1972) have shown that the cloud aerosols are spherical in shape and have a refractive index of  $1.44 (\pm 0.015)$  at a wavelength of  $0.55 \mu\text{m}$ . A cloud candidate must also have equilibrium vapor pressures that are consistent with spectroscopic observations of the abundances of various gases in the Venus atmosphere. Of particular interest is the partial pressure of water vapor near the cloud tops. The most definitive observations of the elusive Venus water vapor features are those of Fink *et al.* (1972), whose results imply a partial pressure of about  $1 \times 10^{-7}$  atm of water vapor near the cloud tops. Finally, cloud candidates should be able to match Venus' reflectivity at visible and ultraviolet wavelengths (Irvine *et al.*, 1968).

In order to make these additional comparisons, we need to specify the cloud temperature. Studies of gaseous absorption spectra (e.g., Young, 1972) and thermal temperature measurements (e.g. Sinton and Strong, 1960; Gillett *et al.*, 1968a) indicate that the cloud top temperature is about  $245^\circ (\pm 15^\circ)\text{K}$ . The cloud-top temperature is needed in evaluating the equilibrium vapor pressures of the cloud material and for determining whether some of the cloud aerosols are in a liquid or a solid state. If they are in liquid phase, they will surely be spherical in shape, whereas if they are in a solid phase, they probably will not be.

We have implicitly assumed up to this point that all of the above properties refer to the same region of the atmosphere and therefore to the same cloud material. This in fact is the case as we now show. Our discussion above of carbon dioxide absorption in the  $2.5\text{--}4.3\text{-}\mu\text{m}$  spectral region indicated that the  $PW$  product representative of at least parts of this region is quite similar to the values that are typical of bands at shorter wavelengths. This result implies that the cloud aerosols responsible for the low reflectivity of Venus in the  $3\text{-}\mu\text{m}$  region are located at about the same

altitudes as the altitudes at which much of the line formation process takes place at the shorter wavelengths. In addition, the value of the cloud-top pressure (or, more exactly, the pressure at optical depth unity) that is inferred from the polarization studies is consistent with the above values of  $PW$ .

Table III is a truth table summarizing the consistency of the various candidate materials with the five sets of data under consideration, "Yes", "No," and "?" entries in Table III connote that the material is, is not, or may be consistent with the observation at the top of the table, respectively. The first column summarizes the discussion of our infrared-reflectivity spectrum and indicates once again the uniqueness of the identification of concentrated sulfuric acid, solely on the basis of these observations. None of the other data are as definitive.

In deriving the other four columns of Table III, we found that a number of ambiguous situations arose. For example, common terrestrial rocks exhibit a significant spread in the values of their refractive indices, with some having values close to the boundary of the polarization results (see, e.g. Pollack *et al.*, 1973). This problem was compounded by the possibility that a number of the entries, e.g. bicarbonate, might contain significant amounts of other mineral materials. Therefore, we put question marks in the index of refraction column next to a number of compounds. A second ambiguity concerned the influence on the ultraviolet spectrum of impurities that might be present in some of the materials. Still a third type of uncertainty arise in judging the sphericity of some of the mineral candidates: One might imagine that these candidates were initially spewed into the atmosphere from volcanic sources and that, as a result, they were initially molten droplets. In this case, when they solidified, they might well remain spherical in shape. Finally, it should be remembered that the assessment of the compatibility of a candidate with the gas spectroscopic data depends on the range of values chosen for the cloud temperature.

TABLE III  
TRUTH TABLE<sup>a</sup>

Material	ir reflectivity	Index of refraction	Vapor pressure <sup>c</sup>	uv reflectivity	Sphericity
Water ice	No	No	No	No <sup>d</sup>	No
Liquid water	No	No	No	No <sup>d</sup>	Yes
Hydrated iron chloride	No	?	Yes	Yes	?
Hydrated silicates	No	?	Yes	Yes	?
Bicarbonate and carbonate	No	?	Yes	No <sup>d</sup>	?
Liquid mercury	No	No	Yes	No	Yes
Mercuric chloride	No	No	Yes	No <sup>d</sup>	No
Ammonium chloride	No	No	Yes	No <sup>d</sup>	No
Ammonium sulfate	No	No	Yes	No <sup>d</sup>	No
Carbon suboxide	No	Yes	No	Yes	Yes
Hydrochloric acid	No	Yes <sup>b</sup>	No	No <sup>d</sup>	Yes
Sulfuric acid	Yes	Yes <sup>b</sup>	Yes <sup>b</sup>	No <sup>d</sup>	Yes
Nitric acid	No	No	No	No <sup>d</sup>	Yes
Hydrocarbons	No	?	?	No	?

<sup>a</sup> References: Grey (1963), Toon and Pollack (1973), Hodgman (1959), Kuiper (1969), Timmermans (1960), Lewis (1972), this paper.

<sup>b</sup> For concentrated solutions.

<sup>c</sup> Cloud temperatures of  $245 \pm 15^\circ\text{K}$  were assumed.

<sup>d</sup> Yes, if we allow for the presence of suitable impurities; no, if there are no impurities.

Based upon a comparison of the properties of sulfuric acid with the then observed properties of the Venus clouds, Sill (1972) and Young (1973) independently suggested that the clouds were composed of concentrated sulfuric acid. Sill inferred a concentration of 86%  $\text{H}_2\text{SO}_4$  by weight, while Young derived a value of 75%. In their analyses, both authors pointed out that laboratory transmission spectra of concentrated sulfuric acid showed it was highly absorbing between 3 and 4 microns; thus, sulfuric acid would be consistent with the low reflectivity of Venus in this spectral region. However, these comparisons with the 3- $\mu\text{m}$  band were considerably clouded by a lack of good observational data throughout the entire band region and a failure to attempt to quantitatively match the observations with a theoretical scattering model.

To reconcile the laboratory spectra of sulfuric acid with the reflectivity spectra of Venus, Young had to adopt a position which contradicted other parts of his analysis. Since concentrated, *liquid* sul-

furic acid has a peak absorption near 3.3  $\mu\text{m}$ , Young was forced to invoke solid sulfuric acid to explain the peak absorption near 3.8  $\mu\text{m}$  in Beer *et al.*'s (1971) measurements of Venus. However, to account for the sphericity of the cloud particles, as implied by the polarization measurements, Young required liquid particles. We have remarked above that carbon dioxide absorption accounts for the 3.8  $\mu\text{m}$  extremum in Venus' spectrum.

Looking at Table III, we see that, while sulfuric acid receives passing grades in the last four columns provided we permit impurities, so do several other candidates. In summary, our aircraft data and their analysis provide strong independent evidence in favor of sulfuric acid clouds. The compatibility of this hypothesis with the other observed properties of the Venus clouds strengthens this inference.

While sulfuric acid aerosols can explain in a straightforward manner almost all the observed properties of the Venus clouds, one must invoke the presence of impurities within the particles to explain the variation

of the cloud's albedo in the 0.2–2.2- $\mu\text{m}$  region. Venus' reflectivity declines somewhat from the visible to the ultraviolet. Also, our results imply a decline from 2.2 to 1.25  $\mu\text{m}$ . If we combine this latter result with an observed shallow decline from about 0.55 to 1  $\mu\text{m}$  (Irvine *et al.*, 1968), we see that a very broad absorption band may be present, centred near 1.1  $\mu\text{m}$ . The invocation of impurities is not an unreasonable hypothesis. Dust particles and other substances could probably readily dissolve in the sulfuric acid particles. In addition, the presence of a decline of the reflectivity of many solar system objects towards the ultraviolet is suggestive of an irradiation effect.

We now consider the question of the concentration of the sulfuric acid. Our observations indicate that the concentration of  $\text{H}_2\text{SO}_4$  by weight is 75% or greater. The ultraviolet and visible observations have no bearing at present on this question. Unfortunately, the index of refraction does not vary significantly over our permitted range, though solutions of concentration less than about 65% have indices of refraction which are too low (Young, 1973). Young showed that only concentrated solutions with values close to 75% or 95% had freezing points that are compatible with the observed cloud temperatures and the inferred sphericity of the cloud particles. However, sulfuric acid solutions have a strong tendency to supercool, so that the acceptable range of concentrations probably encompasses almost all the possible concentrations of sulfuric acid. Finally, the observed water-vapor abundance does potentially place useful limits on the concentration. However, caution must be exercised at present on this piece of data. First, the analysis should be done using a scattering model for the line formation process. Second, while Fink *et al.* (1972) appear to have found water vapor in their spectra, it would be worthwhile to have these observations verified. With these words of caution, we compare the Fink *et al.* (1972) observations with the vapor-pressure curves of sulfuric acid given by Toon and Pollack (1973). At the observed cloud temperatures, concen-

trations of about 85% ( $\pm 10\%$ ) are required. We conclude that while the concentration is at least 75%, it could well be larger.

In an effort to determine more precisely the concentration of the sulfuric acid solution, Young (1974) has investigated the spectral behavior of sulfuric acid in the 750–1200- $\text{cm}^{-1}$  region. He concludes that the absorption characteristics of a 75% solution are in much better accord with the observed spectra of Venus than those of a 90% solution. However, his failure to include the effects of the 960 and 1060  $\text{cm}^{-1}$  carbon dioxide absorption bands throws some doubt on this analysis. The possible importance of these carbon dioxide bands is indicated from an inspection of the laboratory data of Burch *et al.* (1962). Correcting these data to the temperature of the Venus cloud tops and using the *PW* scaling used above, we find that near the band centers the *average* transmission may be diminished by as much as a factor of 2. Thus, even the continuum one derives from intensity values between individual rotational lines may be affected by gas absorption. More detailed calculations are required to assess the importance of these carbon dioxide bands: The 90% solution was rejected because of an absence of a strong feature near 980  $\text{cm}^{-1}$  in the Venus spectra.

We now consider some of the broader implications of our findings. We were originally motivated to consider sulfuric acid as a cloud candidate by analogy to the situation in the Earth's stratosphere. Sulfuric acid is a major component of aerosols in this region of the Earth's atmosphere and, furthermore, the water-vapor content of the stratosphere is quite comparable to that at Venus' cloud tops. It is generally quite difficult to condense a binary compound, such as a solution, because there are two vapor-pressure requirements. Usually at concentrations where one vapor pressure is low enough, the other is not. However, in the case of sulfuric acid, at all concentrations the equilibrium  $\text{H}_2\text{SO}_4$  partial pressure is so low that this requirement is easily met (Toon and Pollack, 1973). Thus, there is really only one stringent requirement, that

set by the water-vapor abundance; this condition can be met in a wide variety of circumstances simply by having a sufficiently concentrated solution. Contrasting cases are provided by the difficulty of condensing nitric acid in the Earth's stratosphere and HCl in Venus' atmosphere. In the case of the Earth, the double vapor-pressure requirement makes it impossible to form nitric acid particles (Toon and Pollack, 1973); while in the case of Venus, it is not possible to form HCl clouds, except perhaps near the temperature minimum in the atmosphere. We conclude that the vapor-pressure behavior of sulfuric acid solutions favors the formation of sulfuric acid particles in the atmospheres of both the Earth and Venus.

Prinn (1973) has proposed that the visible cloud layer on Venus is composed of sulfuric acid droplets formed by rapid photo-oxidation of carbonyl sulfide in the upper atmosphere. His hypothesis was based on the indirect evidence available prior to our observations. Prinn postulates a possible reaction sequence and discusses the chemistry and the atmospheric dynamics leading to the formation of  $H_2SO_4$ .

An alternative mechanism for the formation of sulfuric acid in Venus' atmosphere was proposed by Sill (1972). According to this scheme gaseous HBr is partially decomposed by uv radiation into elemental bromine, which oxidizes such sulfur gases as COS and  $SO_2$  to sulfuric acid. Water vapor is utilized in the oxidation step, with HBr being regenerated at the end of the reaction sequence.

Naturally, to form sulfuric acid solution clouds on Venus, first there must be a source of sulfur-containing gases and water vapor. Venus' atmosphere appears to be of secondary origin and to have resulted from outgassing from the interior of the planet. In the case of the Earth, volcanoes contain a significant amount of sulfur gases and water vapor. The presence of sulfuric acid solution clouds in the case of Venus implies that the outgassed material on Venus also contains a significant amount of sulfur gases and water vapor. This inference is perhaps of some significance in the light of a suggestion made

by Lewis (1972b). Lewis proposed that the temperature conditions in the solar nebula at the time of formation of the terrestrial planets might prevent the condensation of sulfur and water compounds near the orbit of Venus, but not near the Earth's orbit. If this is true, Lewis pointed out that the small but significant difference in the mean densities of the two planets could be understood. While the atmosphere contains very little of the planet's mass, the presence of sulfuric acid clouds may offer some evidence against this hypothesis. On the other hand, Prinn (1973) suggests that, even if Venus formed without sulfur, cometary impacts could supply the amount of sulfur required to explain the presence of an  $H_2SO_4$  cloud layer.

#### CONCLUSIONS

Among the 14 candidates considered, only sulfuric acid clouds with a concentration of 75% or greater are consistent with our observations of Venus in the 2-4- $\mu$ m region. Furthermore, this composition is consistent with a number of other observed properties of the Venus clouds, though one must hypothesize the presence of impurities to explain the smaller variations of Venus' reflectivity between 0.2-2  $\mu$ m. These results apply to the top of the Venus cloud layer, i.e., at an altitude of about 60 km above the surface. Analysis of the results of a photometer experiment carried by the Venera 8 spacecraft (Avdeevsky *et al.*, 1973) indicates that clouds are present down to an altitude of 35 km. Conceivably, the sulfuric acid clouds could extend to this depth; alternatively, there are clouds of different composition at lower altitudes. Distinction between these two possibilities must await future spacecraft missions to probe Venus' atmosphere.

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