

PART II

TERRESTRIAL PLANETS

INFRARED SPECTRA OF VENUS

LOUISE GRAY YOUNG

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., U.S.A.

Abstract. A historical account of observations of Venus and their interpretation is given. The major constituent of the atmosphere on Venus (CO₂) was detected spectroscopically forty years ago, and minor constituents (CO, HF, HCl) have been found more recently. The infrared spectra also provide a means of studying the motions of her cloudy atmosphere. The composition of the clouds has been sought in the reflection spectrum of Venus, and some of the evidence for their nature is discussed.

1. Early Observations of Venus

Venus has been known to possess an atmosphere since 1761. In that year, the Russian astronomer M. W. Lomonosov observed the transit of Venus across the face of the Sun and stated "the planet Venus is surrounded by a considerable atmosphere equal to, if not greater than, that which envelops our earthly sphere." The next reported observation of Venus' atmosphere was made by Schröter (1792) who noted that the horns of the crescent Venus extend beyond a semicircle. When Venus is near inferior conjunction (i.e. when the phase angle i , the angle between the Earth and the Sun as viewed from Venus, is nearly 180°) the horns of her crescent can be seen to extend around the circumference of the planet. Herschel (1793) also remarked on the extension of the horns and wrote "the atmosphere of Venus is probably very considerable ..." Mädler (1849) saw 240° of the circumference of Venus illuminated, while Lyman (1866, 1874) succeeded in observing Venus when she appeared as a luminous ring.

Thus by the mid-nineteenth century Venus was known to have an atmosphere, but its composition remained unknown. Since the Earth and Venus were known to have a similar size and mass, it was logical to expect their atmospheres to be of a similar composition and extent. This notion was not completely dispelled until the Russian spacecraft Venera 4 entered the atmosphere of Venus, and made measurements of its physical and chemical properties.

With the development of the spectroscope, astronomers hoped to find more definite results, and the search for oxygen and water vapor began. The first attempt we know about was made by the astrophysicist Sir William Huggins, and Dr W. A. Miller, a chemist. Huggins (1864) reported that "the light of Venus gives a spectrum of great beauty" but their spectrum failed to reveal any lines not present in the corresponding solar spectrum. He suggested that this was because "the light is chiefly reflected, not from the planetary surface, but from masses of cloud in the upper strata of the atmosphere".

More extensive spectra were observed by Vogel (1874) who reported that telluric absorption features were enhanced in the spectrum of Venus. Tacchini and Ricco (1882) and Young (1885) also reported observations which indicated the presence of

water vapor in the atmosphere of Venus. There was one pitfall that these early observers failed to avoid: the variations in local humidity at their observing site and the different telluric air masses traversed by spectra of the Sun and Venus. On the basis of quite flimsy spectroscopic evidence, Scheiner concluded that "There can therefore be no doubt that the atmosphere of Venus exerts an absorption similar to our own, and hence the nature of the two atmospheres must be similar."

The faintness of the atmospheric lines of Venus indicates that the atmosphere is very thin, or else that the sunlight can penetrate only a short distance into it, being thus reflected from its upper strata. The latter explanation agrees well with other astronomical observations which show a thick envelope of clouds prevents a view of the true surface of the planet. This layer of condensed vapors would be naturally supposed to be situated at a considerable altitude in the atmosphere. Since Janssen's investigations show that the telluric lines are chiefly due to aqueous vapor, we may safely assume that the clouds of Venus consists of condensed aqueous vapor, thus again resembling those of the Earth." Arrhenius (1918) was even bolder: "The humidity is probably about six times the average of that on Earth and three times that in the Congo where the average temperature is 26 °C. The atmosphere of Venus holds about as much water vapor 5 km *above* the surface as does the atmosphere of the Earth *at* the surface. We must therefore conclude that everything on Venus is dripping wet. The vegetative processes are greatly accelerated by the high temperature. Therefore the lifetime of organisms is probably short."

The early observations of the spectrum of Venus have been made visually. A spectrum of Venus was compared with a spectrum of the sky (or of sunlight reflected from the Moon) and the relative intensities of the telluric absorption bands on the two spectra were estimated. Much more accurate measurements can be made at higher resolution when the well-known Doppler effect can be used to separate the absorption lines due to Venus' atmosphere from those of the Earth's atmosphere. Lowell (1905) suggested measuring oxygen and water vapor lines to see whether they were affected by the Doppler shift. V. M. Slipher photographed the spectrum of Venus and the sky, with a dispersion of 50 Å mm⁻¹, and Lowell had this to say: "Here again eye estimates by the writer subscribed to a shift in the α band (of oxygen), the water lines, very faint, concurring; ... As regarded differences in density, none was perceptible between ... the solar and Venusian, either in the oxygen α band or the water vapor lines near (sodium) D. Water vapor is probably non-existent on the illuminated side of Venus. As for oxygen the results above show that the spectroscopic method is hardly a delicate enough in this respect to decide the question." Slipher (1908) added, "Although this attempt has failed to detect aqueous vapor in Mars and Venus, the conclusion should not be drawn that it does not exist in their atmospheres, nor that it will always remain impossible to discover it spectrographically." Slipher continued to search for atmospheric absorption in the spectrum of Venus with negative results. Slipher (1921) wrote, "The high albedo and telescopic appearance of Venus ... seem to me to imply that our view of her is mainly a super-surface one, which may not be appreciably affected by light returned from her surface. And when the marked concentration of

moisture in our air in its lowest stratum is considered, I become cautious about concluding that such results are proof of the absence of water on Venus ... There is telescopic evidence of incomplete light penetration of the atmosphere of Venus, hence we should expect that, because of the probable low-lying position of the moisture on her, its detection would be difficult. The depth of light penetration is obviously important."

An extensive series of measurements of the spectrum of Venus, at high dispersion (3 \AA mm^{-1}), were made at Mt. Wilson Observatory between 1919 and 1921. Initially the spectra were taken to 'check Evershed's results' (St. John and Nicholson, 1920). Evershed (1918, 1919a-c) had made "a long series of measures of Venus and Fe arc spectra, and control plates of sunlight and Fe arc, with the very remarkable result, already indicated in previous work, that the integrated light of the Sun reflected by Venus differs from ordinary sunlight in the mean wave-length of the iron lines being quite appreciably smaller when the angle Venus-Sun-Earth exceeds 90° ." Evershed was "reluctant to accept the Venus result since they seem to prove a recessive motion of solar gases controlled by the Earth."

St. John and Nicholson (1921) found "the main factors producing the displacements (of the solar lines reflected by Venus) are those depending upon the low altitude of Venus at the time of observation. When this effect is eliminated, the remaining residuals, which seem to vary with the relative position of Earth, Venus and Sun are more reasonably correlated with the varying diameter of the planet than with the angle VSE." "The correlation with the altitude at the time of observation points to (atmospheric) refraction as the controlling factor (producing systematic displacements of the solar lines in spectra of Venus) rather than to a repulsive 'Earth effect' acting on the solar vapors as suggested by Evershed ... the observed displacements are caused by unsymmetrical illumination of the slit due to the separation of the visual and photographic images by atmospheric refraction, and ... the unequal illumination is a function of the diameter of the image and the width of the slit."

Having dispelled the mythical Evershed Earth-repulsive effect, St. John and Nicholson then proceeded to look for oxygen and water vapor in their spectra of Venus. Five spectrograms of Venus were taken in the region of the α band of oxygen ($\lambda 6278$) when the relative velocity of Venus and Earth was -12.8 km s^{-1} . This corresponded to a Doppler shift of 0.268 \AA to the violet, an amount sufficient to separate completely the terrestrial components. St. John and Nicholson (1922) reported "no lines are observable where they should appear if produced by oxygen in Venus' atmosphere." They also looked at the oxygen B band, $\lambda 6867$. This band is produced by a much smaller amount of O_2 than the α band and thus furnishes a more sensitive test for O_2 on Venus. King (1922) had shown that 39.4 m of air (or 8 m of O_2) at 72 cm pressure produces faint lines in the B band. Spectrograms of Venus taken when the relative velocity was -10.68 km s^{-1} (or a Doppler shift of -0.245 \AA) and when it was $+11.36 \text{ km s}^{-1}$ (or a Doppler shift of $+0.286 \text{ \AA}$) showed no oxygen absorption in the atmosphere of Venus. The light path through the atmosphere of Venus was estimated to be "7.5 times the radial depth of the layer." Thus if an oxygen layer equivalent to 1 m atm_{stp} were present in the atmosphere of Venus, detectable O_2 lines should have been

observed. Hence an upper limit of $1 \text{ m atm}_{s_{tp}}$ could be set to the amount of O_2 observable on Venus.

Eight water vapor lines ($\lambda 5886\text{--}\lambda 5932$) were examined when the relative velocity of Venus and the Earth was -12.8 km s^{-1} (or a Doppler shift of -0.252 \AA). Again St. John and Nicholson found "no traces of lines due to the planet's atmosphere are discernable on the spectrograms ... there must have been less than 1 mm of water in the layer of the planet's atmosphere traversed by the solar beam ..." They conclude: "These observations indicate that the previous spectroscopic evidence for oxygen and water vapor in the atmosphere of Venus, depending upon visual observations of a change in line intensity, is not reliable, that in fact there is no spectroscopic evidence of the presence of either. On the other hand, they do not show the complete absence of water vapor and oxygen from the planet's atmosphere, but that, to the depth penetrated by the solar beam, they are not present beyond a definite low limit."

A question which bothered St. John and Nicholson, as well as other observers, was how deep into the atmosphere of Venus the sunlight had penetrated before it was reflected back to observers on Earth. Before Russell's investigation (1899) the accepted view was that Venus' atmosphere was much denser than that of the Earth. Russell had shown that the prolongation of the cusps of Venus was mainly due to diffuse reflection of light in the planet's atmosphere. He concluded that there is no satisfactory evidence that the atmosphere of Venus at the apparent surface (cloud top) is more than one-third as dense as the Earth's at sea level. Russell thought the entire height of the atmosphere above the apparent surface might be 50 km and that the pressure there could be one-tenth that of the Earth's atmosphere at sea level.

On the other hand, Claydon (1909) argued for a dense atmosphere at least as extensive as that of the Earth. He assumed a high and heavy layer of pillared cumuli, which would account for the observed features on Venus, with a filmy veil of cirrus above it, which produces the prolongation of the cusps. This model indicated that the reflected sunlight could not have reached any closer to the real surface of Venus than the 43 km level, if her atmosphere was similar to that of the Earth. For in the case of Earth, one only finds 1 m atm of O_2 above the 43 km level. St. John and Nicholson's (1922) failure to detect water vapor did not appear to agree with part of Claydon's model of the Venus atmosphere: "If the dusky markings ... are a transient thinning of a cloudy envelope, it is probable that we there see down to levels at which humidity would be high in an atmosphere so heavily moisture laden that the planet is enveloped in a blanket of clouds ... If, however, the reflecting surface consists of a permanent layer of cirro-stratus, the quantity of water vapor traversed by the reflected beam would be small, as cirro-strati are formed in the upper troposphere where the temperatures are very low ... Reflection from a layer of cirri gives the shortest possible path of light in the planet's atmosphere. The water vapor above the cirrus level may be insufficient for detection by observations on the lines in the rain band."

St. John and Nicholson considered the following alternatives to water vapor clouds: "It is possible that a very small quantity of water vapor would produce an impenetrable haze-bank if the atmosphere of Venus contained minute hygroscopic centers of

condensation capable of producing cloud particles in an atmosphere where the humidity is much below that which otherwise would be essential to cloud formation.” “... it is conceivable that violent atmospheric circulation would cause clouds of dust to be permanent features of the planet’s atmosphere ...” They conclude, “It has been too easily assumed, perhaps, that the atmospheric conditions on our nearest planetary neighbors are similar to those on Earth ... It was long ago suggested by Koene (1856) of Brussels, that all free oxygen may have been formed from carbonic acid in the air. Arrhenius (1908) says that probably all the oxygen of the air owes its existence to plant life. That a similar production of oxygen has apparently not taken place on Venus suggests that some conditions are wanting ... it may be that the exacting conditions for the origin of life have not been satisfied so that the existing atmosphere may consist of other permanent or semi permanent gases such as nitrogen or carbon dioxide.”

Finally, we should mention that St. John and Nicholson assumed that the Doppler shifts due to the rotation of Venus “were assumed to be negligible, as would be the case for the long rotation period shown by Slipher’s (spectroscopic) observations.”

1.1. EARLY OBSERVATIONS OF THE ROTATION OF VENUS

We currently believe that ‘motions’ observed in the clouds of Venus are not directly related to the rotation of the planet, but for many years observers attempted to determine her solid-body rotation by observing cloud features. Spectroscopic studies can, however, reveal the velocity (or wind speed) of the cloud tops. The rotation period of Venus has been determined by radar observations of surface features to be 242.98 ± 0.04 days retrograde (Carpenter, 1970). This corresponds to ~ 117 Earth days for one Venus day (i.e. the time interval between noontimes on the surface of Venus is 117 times as long as between noontimes on Earth).

Barnard (1897) wrote “no other object has caused more controversy and produced more varied testimony in the determination of its rotation period than the planet Venus. This rotation controversy has raged for upwards of two centuries, with fitful periods of quiescence – after some observer more combative than the rest had definitely ‘settled the question’ only to break out again with renewed virulence when a new champion for rotational honors entered the field.

“The periods assigned to the planet vary all the way from 23 or 24 hours to 225 days. One of the short period men has gone so far as to produce a period, derived from drawings made a few days apart, with a decimal running to the ten-thousandth of a second, which ought certainly to be convincing enough, as a smaller subdivision of time would be an insensible quantity and ought never to be stickled for in determining the duration of a planetary day.

“These discrepancies are due in the main to the difficulty – from various causes – of seeing markings which really exist on the surface of Venus.”

Among the observers active at the time Barnard was writing were G. V. Schiaparelli and C. Flammarion. Schiaparelli’s (1890) opinion was “the planet makes one rotation in 224.7 days – that is to say, in a period exactly equal to the duration of its sidereal revolution about the Sun ... The rapid variations in the aspect of the planet (and espe-

cially in the horns of its crescent), which have been frequently noticed to repeat themselves in a period of about 24 hours cannot be adduced to support the hypothesis of a rotation of about one day. Such variations arise from atmospheric causes, which tend to repeat themselves in daily period." Flammarion (1894) had observed white features at the poles of Venus remarking that "the general tone of the disc of Venus is a bright yellow." He argued, "If these whitened poles are not an illusion, and if they represent snow or cloud, their existence would be inexplicable in the hypothesis where the planet rotates in the same time as it revolves. In fact, in the case where it always presents the same face to the Sun, the maximum cold would be in the hemisphere opposed to the Sun, and the maximum temperature towards the center of the illuminated hemisphere; all the circumference of the illuminated hemisphere would be in the same condition of climate ... The observation of spots are insufficient to determine the period of rotation, but they seem to indicate that it is not far from 24 hours."

Belopolsky (1900) observed Venus spectroscopically and found an equatorial velocity of $v = 600 \pm 300 \text{ m s}^{-1}$ indicating a rotation period of less than one day. Slipher (1903) observed Venus at superior conjunction and found velocities ranging from 90 m s^{-1} (direct) to 120 m s^{-1} (retrograde) with an average velocity of $19 \pm 12 \text{ m s}^{-1}$ (direct). He concluded "that there is no evidence that Venus has a short period of rotation." Fifty years passed before another attempt was made to determine the rotation of Venus spectroscopically. Richardson's (1958) results, based on 102 measurements, indicated a mean velocity of $32 \pm 33 \text{ m s}^{-1}$ (retrograde). His measured velocities ranged from 900 m s^{-1} (direct) to 900 m s^{-1} (retrograde). Richardson found values in the range $100\text{--}200 \text{ m s}^{-1}$ (retrograde) occurred with the greatest frequency and the measurements appeared to follow a normal error distribution.

1.2. PHOTOGRAPHS OF VENUS

Wright (1927) took a number of photographs of Venus at both infrared (7600 \AA) and violet wavelengths. Venus was featureless in the infrared photographs but showed bright streaks or bands in the violet. He remarked "It appears reasonable to assume that the violet photographs represent an upper level of the atmosphere of Venus and that the hazy markings ... are therefore atmospheric phenomena. In that case they are probably variable in form, and, as they are the only planetary markings found at the time, it seems likely that markings reported on occasion by observers with the telescope are of this nature. This would explain the numerous discrepancies in the observations of these observers." Ross (1928, 1931) reported similar results: features showed up in photographs he made through an ultraviolet filter but photographs of Venus made through blue, red and infrared filters gave no trace of the markings. Ross (1928) remarked that "there is nearly always a complete change of cloud formation from day to day" in the ultraviolet photographs of Venus. On the interpretation of his photographs, Ross had this to say:

"Granted that Venus has an atmosphere which hides the surface from visual observation, it is normally to be expected that photographs taken in infrared light, which would perhaps penetrate the atmosphere, might disclose surface features, just as

during the great war photographers were able to take pictures of the Earth's surface from points several miles above it by the use of infrared light ... But in photographing Venus, this does not appear to hold, the short waves now being the useful ones." Ross suggests the following explanation: ... "the apparent white surface which we see is imagined to be a uniform shell of light cirrus clouds overlying a dense yellow atmosphere. On occasions of violent atmospheric disturbance the uniform cloud-covering is broken up, and we see the underlying yellow atmosphere to which are due the dark markings seen visually and photographically. Or the cirri may in certain regions be piled up in heavy masses, again seen visually and photographically as brilliant white clouds.

"The observed visual albedo of Venus is not out of harmony with the hypothesis of a covering of light cirrus clouds. The coefficient of reflection of dense white clouds is 78%. According to Russell (1916) the coefficient of reflection of the outercloud-mantle of Venus is 49% ... The clouds on Venus thus have considerably less reflectivity than white clouds on Earth, a fact in harmony with the hypothesis of a scarcity of water vapor ..."

Ross was the first person to make systematic observations of Venus in ultraviolet light, which clearly revealed the day-to-day variations in her atmosphere. Twenty years went by before professional astronomers again looked for the dark markings in ultraviolet photographs. Observations were made by Dollfus (1953, 1955a, b) in the 1940's, Kuiper (1954) in 1950 and Richardson (1955) in 1954. In 1957 Boyer began a long series of photographic observations of Venus. He noticed that a dark cloud feature recurred on photographs taken 4 days apart. This suggested the possibility of a retrograde rotation of the upper clouds with a 4 day period (Boyer and Camichel, 1961). Boyer and Guérin (1966) then obtained sequences of ultraviolet photographs, at intervals varying from 2 to 6 hours, and the dark cloud markings were observed to move. Measurements of the photographs indicated they moved with an equatorial mean velocity of $-105 \pm 11 \text{ m s}^{-1}$ (Boyer and Guérin, 1969); the measured velocities of cloud features varied from -68 m s^{-1} to -229 m s^{-1} . Smith (1967) confirmed the rapid cloud motions but he commented, "... investigation of a large number of our own photographs taken since 1959 has failed to reveal any *well-defined* repetitive patterns, although somewhat similar (cloud) formations often reoccur at 3-to-5 day intervals. Because of the uncertainties in the lifetimes of Venus cloud formations, there is no assurance that similar patterns reappearing after 4 or 5 days are in fact the original clouds. ... Indeed, some of our 1967 plates show strikingly similar cloud patterns at intervals of only 2 days although individual cloud displacements during several hours on these same dates clearly exhibit motions corresponding to a period of 5 days."

Scott and Reese (1972) reported, "The ultraviolet markings appear to be randomly distributed and quite ephemeral in nature, rarely enduring in a recognizable pattern for more than 20 days and usually much less." They found cloud velocities which varied from -66 to -127 m s^{-1} at the equator, with a mean equatorial velocity of $-97.7 \pm 6.4 \text{ m s}^{-1}$, a mean sidereal rotation period of 4.57 ± 0.30 days retrograde, with

individual periods ranging from 3.5 to 6.8 days. Caldwell's (1972) observations indicated a sidereal rotation period of 4.50 ± 0.02 days, while Boyer and Guérin's study indicated a period of 4.067 days. The period for cloud features, and hence the wind velocities in the atmosphere above the clouds, may vary from day-to-day, which may account for the apparent lack of agreement between the Venus observations made at different observatories.

1.3. RADIOMETRIC OBSERVATIONS

Pettit and Nicholson (1923, 1924, 1927, 1930, 1936), Menzel (1923), Menzel *et al.* (1926), and Coblenz and Lampland (1924, 1925a, b, 1927) were among the first to measure the thermal radiation emitted by Venus. Pettit and Nicholson (1927) reported "Two methods of estimating the temperature of emission of the radiation from the dark side agree in assigning a value near 250 K. This is consistent with what might be expected from radiation emitted by a cirrus cloud covered atmosphere." They found the same temperature on the bright side of the planet which indicated the temperature was uniform over the planet. Later radiometric observations of Venus were made by Sinton and Strong (1960) who reported a brightness temperature of 234 K. They also found very little (2 K) difference in temperatures between the bright and the dark side of the disc. Chase *et al.* (1963) reported an average temperature for Venus of 225 ± 2 K as measured by the Mariner II radiometer; they had difficulties in the calibration of their instrument and this value is not too reliable as a result. Murray *et al.* (1963a) also experienced difficulties in obtaining a good absolute calibration of their brightness temperature of Venus measured in the 8 to 14 μ wavelength region. Their measurements indicated a temperature of 208 ± 2 K at the center of the disc. The differential accuracy of brightness temperatures measured by Murray *et al.* was about $\frac{1}{2}$ K, however, and their high resolution maps of the temperature distribution over the planet also show the absence of a strong night-to-day effect.

Sinton (1964a, b) had made a series of radiometric observations of Venus from 1958 to 1962 and concluded that "Venus does not exhibit an appreciable periodic variation in its infrared temperature (of 232 K) and that its atmosphere is uniformly opaque from 3 to 30 μ ."

1.4. OBSERVATIONS OF MICROWAVE RADIATION FROM VENUS

The investigation of thermal radiation from planets, at radio wavelengths, began comparatively recently. Microwave emission from Venus was first observed in 1956 by Mayer *et al.* (1958). They made observations, at a wavelength of 3.15 cm, over a period of nearly two months. Mayer *et al.* reported an apparent blackbody temperature which varied from 630 ± 110 K (m.e.) to about 560 ± 73 K (m.e.) near inferior conjunction. "Two single observations at 9.4 cm wavelength suggest the bulk of the radiation follows a thermal spectrum, but, the accuracy of these measurements is low." Since that time many more measurements have been made, at wavelengths from 0.3 to 40 cm. These measurements have been summarized by Barrett and Staelin (1964), Dickel (1967), Kuzmin (1967), and Pollack and Morrison (1970).

The microwave brightness temperature was much higher than had been anticipated. The simplest explanation of the measurements is to assume that the atmosphere is almost transparent at these wavelengths and that the temperatures refer to the surface and lowest levels of the atmosphere. (Sagan 1960; Barrett, 1961; Barrett and Staelin, 1964). This explanation was unpopular since there was a general belief that Venus was not drastically different from the Earth. With the exception of Wildt's (1940a, b) suggestion, that the surface temperature of Venus might be as high as $366\text{ K} < T_s < 408\text{ K}$, there had been little observational evidence to indicate that the surface of Venus might

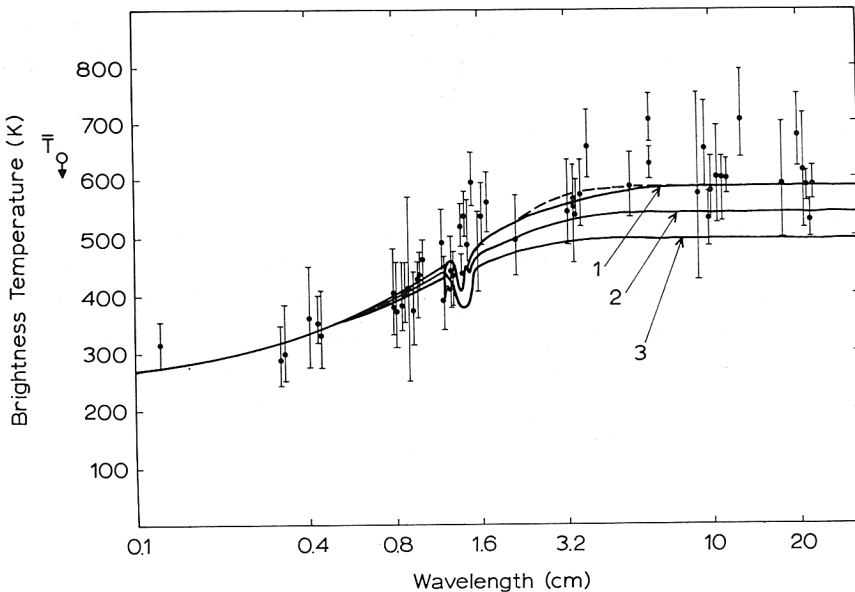


Fig. 1. Brightness temperature of Venus in the microwave region. The solid curves were computed for surface temperatures of 650 K (1), 600 K (2), and 550 K (3) assuming a surface pressure of 20 atm; the dashed curve is for a surface pressure of 70 atm. The curves were computed for a mixing ratio of 0.4% H_2O in the atmosphere and show the 1.38 cm absorption line of water. (From Kuzmin and Vetukhnovskaya, 1968, *J. Atmospheric Sci.* **25**, 546.)

not be suitable for man to explore. Since the obvious interpretation of the data was unpalatable, there arose a number of fascinating hypotheses to 'explain' the observations (Jones, 1961; Priester *et al.*, 1962; Tolbert and Straiton, 1962; Danilov and Yatsenko, 1963; Danilov, 1964; Kuzmin, 1964; Vakhnin and Lobedinskii, 1966; Plummer and Strong, 1966, 1967; Drake, 1967). Unfortunately, none of the non-thermal 'explanations' were capable of agreeing with *all* the observational data. On the other hand, the original assumption of Mayer *et al.* (1958) that the microwave brightness temperature was due to thermal emission has proven to be correct.

Model atmosphere calculations assuming a high surface temperature had been made by Sagan (1960, 1967a, b), Barrett and Staelin (1964), Ho *et al.* (1966), and Young and Gray (1968) at a time when the reason for the high microwave temperature was

disputed. The calculations all agreed that the surface pressure had to be $p_s > 10$ atm. Sagan (1967a, b, 1968) had shown that it was possible to deduce a high surface temperature ($T_s \approx 700$ K), [based on the difference between the optical and radar diameters of Venus, the known temperature at the cloud top and an assumed adiabatic temperature gradient between the clouds and the surface] independent of the microwave measurements. It was only after the *in situ* measurements of Venera 4 and Mariner 5 were reported (Avduevsky *et al.*, 1968; Kliore *et al.*, 1967; Kliore and Cain, 1968; Wood *et al.*, 1968; Eshleman, 1968) that the idea of a surface temperature for Venus $T_s \sim 500$ K was widely believed. The microwave measurements of brightness temperature were finally taken at face value, ten years after the first observations had been reported. The measurements from Venera 5, 6, and 7 confirmed the high surface temperature. Venera 7 measurements indicated a surface temperature of $T_s = 747 \pm 20$ K with a surface pressure, $p_s = 90 \pm 15$ bars (Marov, 1972).

1.5. OBSERVATIONS OF THE POLARIZATION OF SUNLIGHT REFLECTED BY VENUS

Measurements of the polarization of reflected sunlight are another means of studying a planetary atmosphere. They provide a reliable method of determining whether an atmosphere is clear, hazy or covered by an optically dense cloud cover. Furthermore, one can determine whether the cloud particles are spherical or of irregular shape, an estimate of the particle size distribution and information about the refractive index of the cloud particles. Regardless of the particle shape, the polarization can be used to separate the contribution of the gas molecules in the atmosphere (which follows a Rayleigh scattering law with optical depth, τ , varying with wavelength λ as λ^{-4}) from the contribution of the cloud particles (which is much less strongly wavelength dependent, according to Mie theory).

The first accurate measurements of the polarization of sunlight reflected from Venus were made in 1922 by Lyot (1929). Lyot also made laboratory measurements and noted that the primary effect of multiple scattering was to reduce the amount of polarization without changing the general shape of the polarization curve. The amount of polarization observed by Lyot was small, but his measurements were very accurate. Lyot (1929) found that his visual observations of Venus were in reasonably good qualitative agreement with clouds composed of water (refractive index $n_r \sim 1.33$) drops with a radius $r \sim 1.25 \mu$.

The comparatively low temperatures measured radiometrically for Venus suggested the idea that the clouds of Venus could be composed of water and still the atmosphere might contain very little water vapor above the clouds. This notion still has its proponents.

Like so many other techniques for observing Venus, polarization measurements were neglected for many years. Dollfus (1955a, b) resumed observations with the Lyot visual polarimeter and noted that the polarization varied from one point to another on the disc of the planet. Dollfus also noted that the polarization varied from day-to-day, over a particular location on the planet, on a time scale similar to the variation in the cloud features observed in ultraviolet photographs. In addition to his visual

observations, Dollfus (1958, 1963a, b, 1966) also measured the polarization photoelectrically in the infrared. Subsequent observations of the polarization on Venus were made using colored filters which spanned the wavelength range from 9900 Å in the infrared to 3590 Å in the ultraviolet. (Gehrels and Samuelson, 1961; Coffeen, 1968; Coffeen and Gehrels, 1969; Dollfus and Coffeen, 1970). Coffeen, (1969) compared the observa-

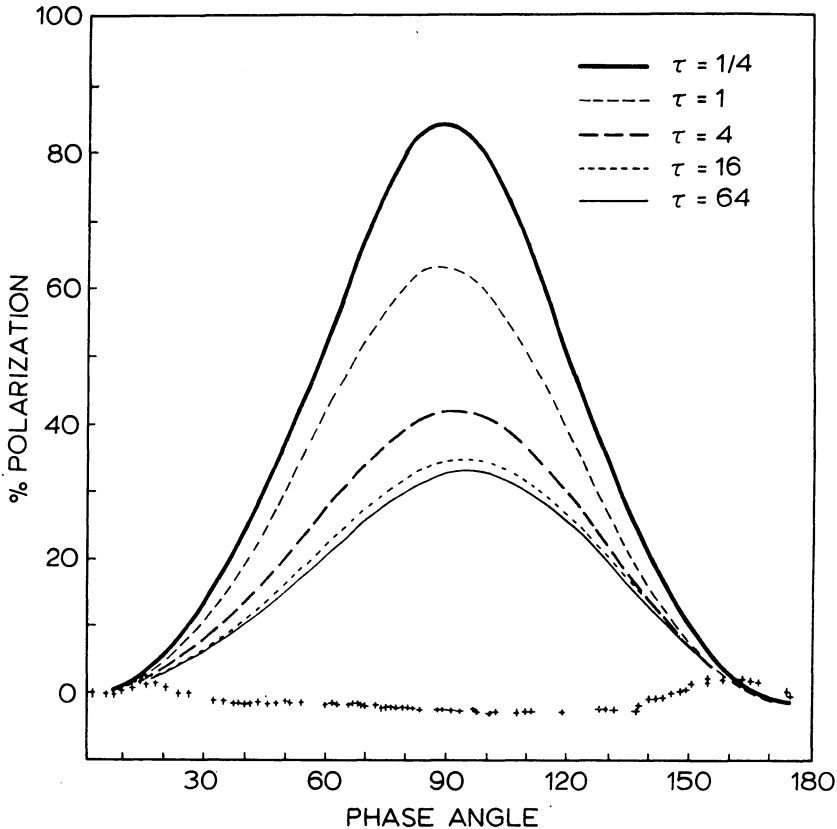


Fig. 2. Theoretical curves of the polarization calculated for Rayleigh scattering atmospheres as a function of the total scattering optical depth. The crosses represent Lyot's measurements of the polarization of visible light reflected from Venus. The lack of agreement between the observations and a Rayleigh scattering atmosphere is apparent. (From Hansen and Arking, 1971, *Science* 171, 669).

tions of Coffeen and Gehrels (1969) with calculated values of the polarization due to the single-scattering of light by spherical particles. Coffeen concluded that the particles had an index of refraction $1.43 \leq n_r \leq 1.55$ and a particle radius, $r \sim 1.25 \mu$.

Russian spacecraft which have entered the atmosphere of Venus have shown that her atmosphere is considerably more massive than that of the Earth. The pressure at the surface of Venus is 90 ± 15 bars and the temperature is 747 ± 20 K (Marov, 1972; Avduevsky *et al.*, 1970). This means that the temperatures of the clouds measured

radiometrically (and spectroscopically) refer to some high level in the atmosphere. Similarly, it means that the polarization measurements refer primarily to photons which have been multiply scattered within the atmosphere rather than being reflected from the surface. As a result, the complete theoretical interpretation of the observa-

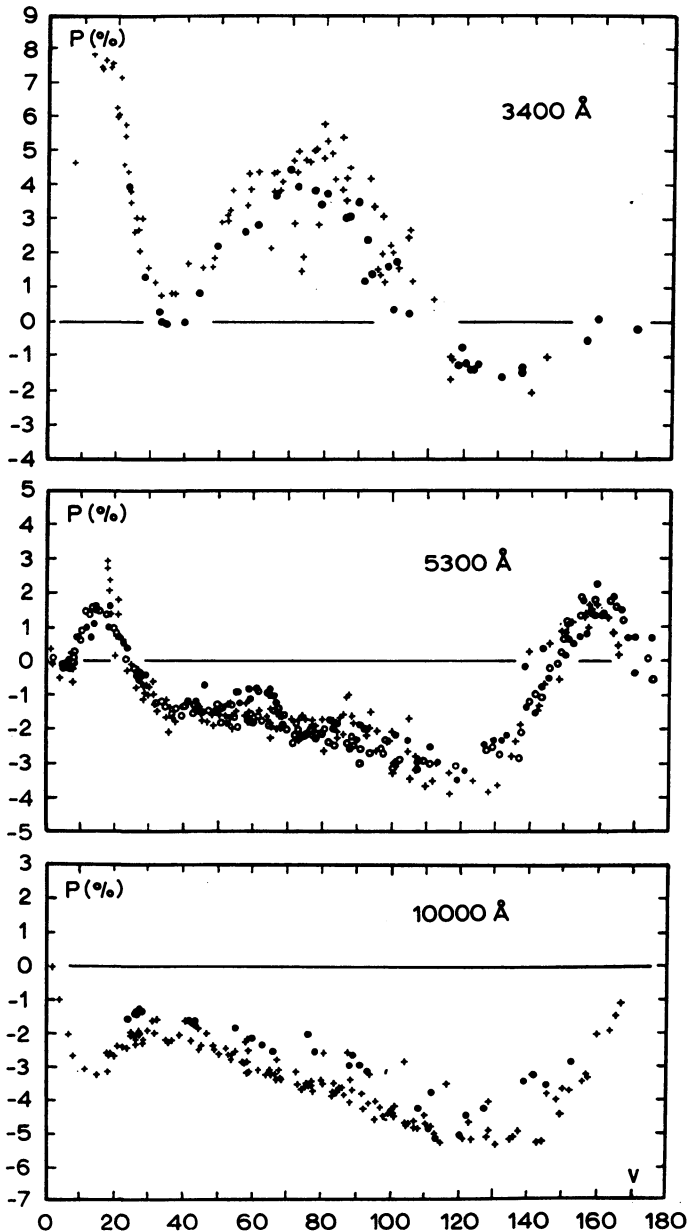


Fig. 3. Observations of the polarization of sunlight reflected from Venus at various wavelengths as a function of phase angle. (From Dollfus and Coffeen, 1970, *Astron. Astrophys.* **8**, 251.)

tions must be based on solutions of the radiative transfer equation. Exact solutions are available for a Rayleigh scattering atmosphere (Chandrasekhar, 1950), i.e. when the radius of the scatterers, r , is much smaller than the wavelength of the light being scattered. However pure Rayleigh scattering produces much more polarization at visible wavelengths than is observed for Venus.

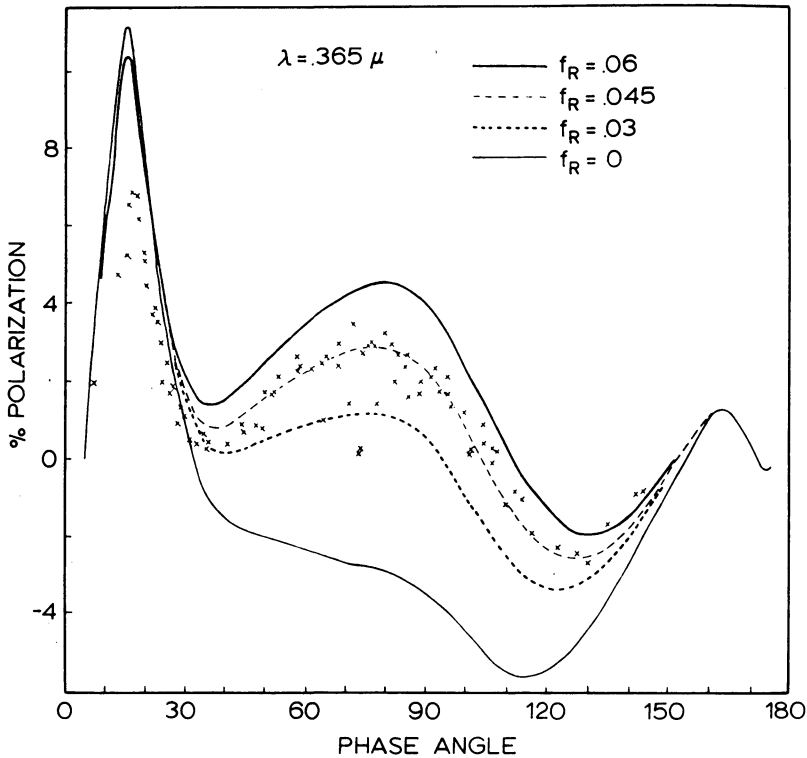


Fig. 4. Theoretical curves of the polarization in the ultraviolet for particles with an index of refraction $n_r = 1.46$ and a radius of 1.1μ for different fractions of Rayleigh scattering, f_R . The crosses represent measurements of the polarization of Venus made by Coffeen and Gehrels. A value of $f_R = 0.045$ implies that the pressure in the clouds where the optical depth is approximately unity is about 50 mb. (From Hansen and Arking, 1971, *Science* 171, 669.)

Coffeen (1969) found an upper limit to the Rayleigh scattering optical depth of $\tau \leq 0.072$ (in the ultraviolet). For a carbon dioxide atmosphere this meant the upper limit to the amount of gas above the clouds was 0.4 km atm or the cloud-top pressure was $p_c \leq 55$ mb. Subsequent calculations by Hansen and Arking (1971) indicated that the fraction of Rayleigh scatterers was $f = 0.045$ (or that the pressure at the cloud tops, $\tau = 1$, is $p_c \leq 35$ mb). Observations indicate the polarization of Venus in the ultraviolet is variable, and the cloud tops appear to occur at pressure levels between 30 and 60 mb based on this data (see also Sagan and Pollack, 1969). The recent analysis of the polarization data by Hansen and Arking indicated that most of the cloud particles

“must be spherical” and “the mean particle radius is $r = 1.1 \pm 0.1 \mu$.” They found that “the dispersion in particle sizes is amazingly small; this result is unexpected for dust, but it is not unusual for a liquid ... The particle shape and the dispersion of particle sizes, taken together, strongly suggests that the cloud particles are liquid.” Hansen

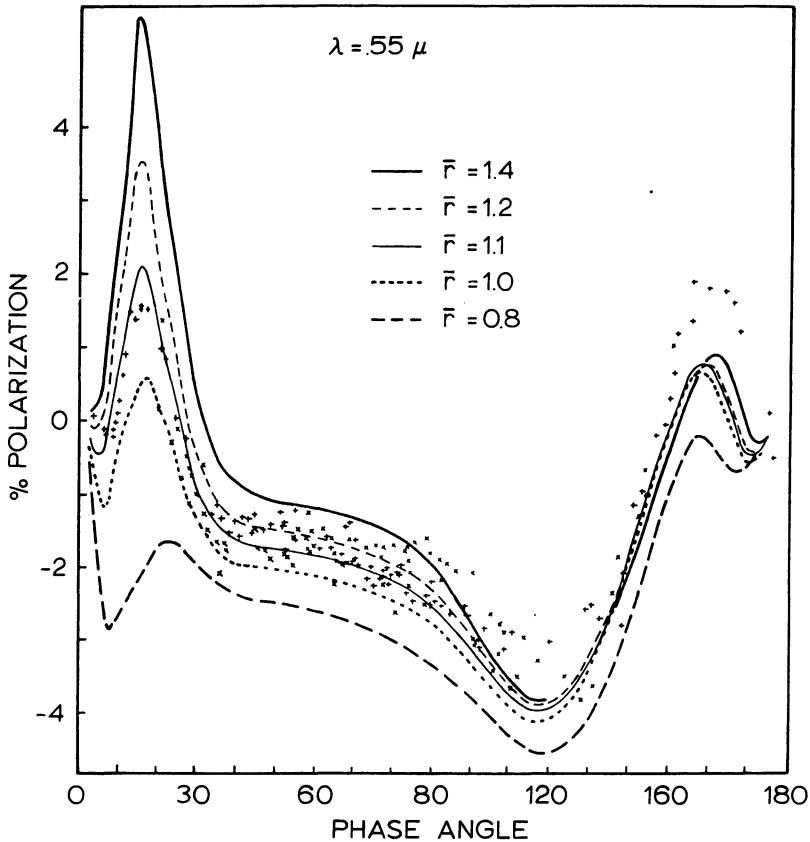


Fig. 5. Theoretical curves of the polarization in the visible for particles with an index of refraction $n_r = 1.45$ and a fraction of Rayleigh scatterers of $f_R = 0.045$ for several values of the mean scattering radius, \bar{r} . The crosses represent Lyot's measurements of the polarization of Venus. (From Hansen and Arking, 1971, *Science* 171, 669.)

and Arking reported, "... the best fit to the observations occurs with a refractive index which decreases from $n_r \sim 1.46$ in the ultraviolet to $n_r \sim 1.43$ at $\lambda = 0.99 \mu$; the uncertainty in n_r is 0.02 at each wavelength."

These results for the refractive index rule out the possibility that the upper clouds of Venus can be composed of pure liquid water or ice. Since the visible clouds are composed of particles with a single index of refraction (as can be seen from the presence of a sharp rainbow in the ultraviolet data) they can not be composed of a mixture such as dust and H_2O . (If there were two or more cloud layers with different

refractive indices, or different particle sizes, then features due to each type of particle would be present in the polarization data). Hansen and Arking's results stringently narrow the list of possible material composing the visible clouds of Venus. They also rule out many of the materials that have been proposed for the composition of the clouds. Table I lists the refractive index of some of the materials which have been, or could be, suggested for the cloud particles.

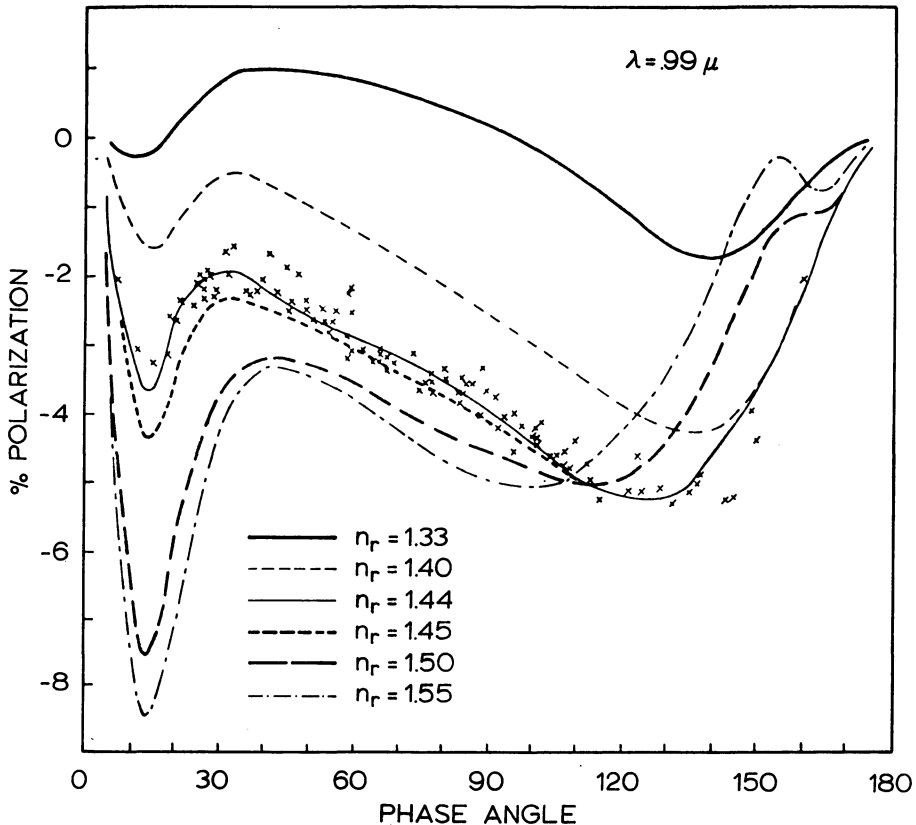


Fig. 6. Theoretical curves of polarization in the near infrared for spherical particles with different indices of refraction. The crosses represent the measurements of the polarization of Venus made by Coffeen and Gehrels. (From Hansen and Arking, 1971, *Science* 171, 669.)

1.6. COMPOSITION OF THE CLOUDS OF VENUS

The early observations of Venus had given rise to the notion that the clouds of Venus were aqueous. Then it became fashionable to suppose they were composed of dust. Wildt (1940a, b) was the first to propose a more exotic chemical composition for the clouds: polymerized formaldehyde. Wildt noted "that the partial pressure of H_2O in Venus' atmosphere must be far below that required for saturation and condensation.

TABLE I
Refractive indices

H ₂ O(<i>s</i>)	1.31	Na ₂ SO ₄	1.48
H ₂ O(<i>l</i>)	1.33	NH ₄ ClO ₄	1.48
D ₂ O(<i>l</i>)	1.33	FeSO ₄ .7H ₂ O	1.48
NaF	1.34	Na ₂ SO ₄	1.48
KF	1.36	KCl	1.49
C ₂ H ₅ OH(<i>l</i>)	1.36	K ₂ SO ₄	1.49
HNO ₃ (<i>l</i>)	1.40	C ₆ H ₆ (<i>l</i>)	1.50
HCl(<i>l</i>)	1.41	CaCl ₂	1.52
SO ₂ (<i>l</i>)	1.41	(NH ₄) ₂ SO ₄	1.52
H ₂ SO ₄ (<i>l</i>).2H ₂ O	1.41	FeSO ₄ .5H ₂ O	1.53
H ₂ O ₂	1.41	NaCl	1.54
CaF ₂	1.43	SiO ₂ (quartz)	1.55
Na ₃ PO ₄ .12H ₂ O	1.43	MgSO ₄	1.56
MgSO ₄ .7H ₂ O	1.43	FeCl ₂	1.57
H ₂ SO ₄ (<i>l</i>)	1.44	Mg(OH) ₂	1.57
ClSO ₃ H	1.44	CaSiO ₃	1.62
C ₃ O ₂ (<i>l</i>)	1.45	CS ₂ (<i>l</i>)	1.63
Na ₂ B ₄ O ₇ .10H ₂ O	1.46	NH ₄ Cl	1.64
NaH ₂ PO ₄ .H ₂ O	1.46	CaCO ₃	1.65
Al ₂ O ₃ SO ₃ .9H ₂ O	1.46	AgNO ₃	1.73
CCl ₄ (<i>l</i>)	1.46	MgO	1.74
Al ₂ (SO ₄) ₃	1.47	CaO	1.84
ZnSO ₄ .7H ₂ O	1.47	HgCl ₂	1.86
SiO ₂ (tridymite)	1.47	Hg ₂ Cl ₂	1.97

Consequently, the concept that the visible surface of Venus consists of a layer of clouds of the same nature as terrestrial ones has to be abandoned, and it appears necessary then to account for the high albedo of the planet in a different way. Gerasimovič (1937) demonstrated conclusively that the only model of Venus' (visible) surface which admits of an explanation both of the absolute brightness of the planet and of its phase curve is a stratum of large scattering particles, which he believes to be products of condensation, without further specifying their character." Wildt continued, "the extreme paucity, if not complete absence, of free oxygen is obviously related to the lack of water on Venus ... The absence of O₂ would deprive Venus of the protection this gas exerts against ultraviolet sunlight. Carbon dioxide and water vapor would be decomposed photochemically, and formation of formaldehyde would follow." Wildt searched for spectroscopic evidence of CH₂O on Venus, and saw none; he found an upper limit of 0.3 cm atm. "This result would seem to refute the alleged accumulation of formaldehyde at Venus' surface. However, gaseous formaldehyde is extremely susceptible to polymerization and precipitation in solid form. Therefore the spectroscopic test refers only to the small amount of gaseous CH₂O in equilibrium with the solid phase." Wildt (1942) later learned that "the vapors of linear formaldehyde polymers are monomeric formaldehyde" and a large fraction (92%) of the polymer clouds would be CH₂O. Thus Wildt's hypothetical plastic clouds on Venus were ruled out on the basis of his own observations.

Van de Hulst (1952) suggested that Lyot's polarimetric observations might be fit as well by small particles of SiO_2 as by H_2O droplets, but the index of refraction of quartz (1.55) is much larger than that found by Hansen and Arking (1971). The suggestions made by Suess (Kuiper, 1952) that the clouds could be composed of salts (NaCl , MgCl_2) also is ruled out by their high refractive index and the requirement that the cloud particles be liquid droplets.

Menzel and Whipple (1955) suggested that "oceans completely covering the surface of Venus could produce H_2O clouds with the general and detailed characteristics observed in the Venusian atmosphere." They based their arguments on Lyot's polarization measurements, the radiometric observations of Sinton, and the fact "that -39°C (234 K) is precisely the temperature assumed by many high-level cumulus clouds on the Earth, because this temperature is the lowest at which water can still exist in the liquid state. The droplets are super cooled but none the less liquid." Menzel and Whipple argued that the comparatively high surface temperatures suggested by Wildt (1940) of "366 K to 408 K appears to be denied by Sinton's measurements." We now know, from the Venera Spacecraft measurements, that the surface temperature of Venus is close to 740 K, much hotter than Wildt had suggested. However the idea that the planet Venus is significantly different from the Earth, and the idea that the radiometric temperatures measured in the infrared was not too much different from the surface temperature, were not to be given up easily.

Öpik (1955) disputed the hypothesis of water clouds. He argued that if the clouds were H_2O , the sunlit half of Venus should be "covered with cumulo-nimbus clouds of varying contours, producing contrasting surface markings which have not been observed. The monotony of the sunlit half of Venus would be more in accord with an indifferent haze or smoke of mineral origin, than with water clouds carrying up almost explosive amounts of latent heat." Öpik suggested that "there may be various kinds of dust, some of which may reveal a similar polarization effect to that caused by water clouds, even if they have not the same chemical composition." "It should be emphasized, in view of the negative outcome of the direct spectroscopic proof, the *approximate* agreement of the reflecting power and polarization curve of Venus with that for clouds of water droplets can not be attributed much weight" (Öpik, 1956).

To paraphrase Barnard, nothing has aroused more controversy and produced more varied testimony than the composition of the clouds of Venus. The controversy has raged with fitful periods of quiescence – only to break out again with renewed virulence. As we appear to be writing this in a quiescent period, it may be useful to recall the legions who have rallied to the defense of aqueous clouds on Venus and those who have opposed them. It is not the intent to give here a blow-by-blow account of all the arguments, pro and con, for water clouds. Table II lists some of the participants involved in the debate. The arguments in support of water clouds rely on the comparatively large amounts of H_2O detected spectroscopically by Bottema *et al.* (1964b), the measurements of H_2O by the spacecraft Venera 4 (Vinogradov *et al.*, 1970a, b), the similarity of the spectrum and polarization data to telluric water clouds, and the need of an additional substance to provide enough of a greenhouse effect to

TABLE II
Aqueous clouds on Venus?

Pro	Con
Vogel (1874)	Slipher and Edson (1939)
Tacchino and Ricco (1882)	Wildt (1940b)
Claydon (1909)	Kuiper (1952)
Arrhenius (1918)	Kuiper (1954)
Ross (1928)	Hoyle (1955)
Lyot (1929)	Öpik (1956)
Menzel and Whipple (1955)	Kuiper (1962)
Sagan (1960)	Moroz (1963)
Dollfus (1963a, b)	Sagan and Kellogg (1963)
Deirmendjian (1964)	Chamberlain (1965)
Bottema <i>et al.</i> (1964a, b, 1965a, b)	Espinola and Blau (1965)
Strong (1965)	Kuiper (1967)
Plummer and Strong (1965)	Kuiper and Forbes (1967)
Ohring (1966)	Rea and O'Leary (1968)
O'Leary (1966)	Coffeen (1968)
Pollack and Wood (1968)	Belton <i>et al.</i> (1968)
Pollack and Sagan (1968)	Lewis (1968a, b 1969)
Hansen and Cheyney (1968)	Hunten and Goody (1969)
Sagan and Pollack (1969)	Kuiper (1969)
Plummer (1969)	Rasool (1970)
Ohring (1969)	Schorn and Young (1971)
Pollack (1969)	Veverka (1971)
Plummer (1970)	Lewis (1971a, b)
O'Leary (1970)	Hansen and Arking (1971)
	Fink <i>et al.</i> (1972)
	Regas <i>et al.</i> (1972)

maintain the high surface temperature. The arguments against water clouds rely on the comparatively small amounts of H₂O detected spectroscopically by other observers, the fact that the refractive index of the cloud particles is significantly larger than that of liquid water or ice, and the contention that no additional substance is required to produce a greenhouse effect (Danielson and Solomon, 1966). It appears that the question of aqueous clouds will only be definitely settled by *in situ* measurements on the clouds of Venus. Some of the more imaginative suggestions for the cloud composition can be dealt with in a less ambiguous way.

Hoyle (1955) suggested that the negative results of the spectroscopic search for water vapor could be explained if a great excess of hydrocarbons existed on the primitive planet Venus. He surmised that the surface is now covered with the remainder of the hydrocarbons, and that the cloud layer is composed of smog. This hypothesis about the nature of the clouds of Venus was not exactly new. Velikovsky (1950) had made a similar prediction based on his interpretation of ancient myths and documents of varying antiquity. Velikovsky's version of cosmogony differs radically from that of physical scientists (Newton's Law of Gravitation doesn't hold, angular momentum isn't conserved, etc.) and the accuracy of his research has been questioned (Payne-Gaposchkin, 1950; Margolis, 1964). Mintz (1961), Kaplan (1963), and Robbins

(1965) also postulated hydrocarbon clouds. Kaplan said, "An attractive possibility is that the clouds are mostly composed of organic compounds, many of which have sufficiently high condensation or polymerization temperature: about 1 m atm_{stp} of almost any gaseous compound containing a C—H bond would be sufficient to close a spectral window around 3.5 μ , which would otherwise allow more radiation to escape from the surface than can possibly be compensated by incoming sunlight." These postulated hydrocarbons would explain two observational results: the low albedo of Venus in the 3–4 μ spectral region and the high surface temperature which is believed to be maintained by a greenhouse effect. One difficulty with the suggestion of hydrocarbons is the absence of an absorption feature near 2.4 μ in the spectrum of Venus. Plummer (1969) has pointed out that "Each hydrocarbon (from methane through the hydrocarbon waxes and tars) absorbs infrared radiation in a band of wavelengths centered between 2.3 and 2.5 μ , the position varying somewhat with molecular structure." Earlier searches for hydrocarbons in the spectrum of Venus had also been unsuccessful. Kuiper (1952) estimated there could be no more than 0.5 cm atm_{stp} of C₂H₆, 1.5 cm atm_{stp} of C₂H₄ or 10 cm atm_{stp} of CH₄ above the clouds of Venus and remain undetected in his low resolution spectra of Venus. The high resolution spectra of Connes *et al.* (1967) failed to reveal any detectable lines of CH₄, CH₃Cl, CH₃F, C₂H₆ or HCN; they estimated that there could be no more than 0.3 cm atm of any of these gases above the clouds. Thus all of the spectroscopic data are unfavorable to clouds composed of hydrocarbons.

Mueller (1964), Dayhoff *et al.* (1967), and Lewis (1968a, b) have placed stringent theoretical upper limits on various hydrocarbons through considerations of chemical equilibrium. To quote Lewis (1969), "Perhaps the most effective criticisms of these suggestions are based on (1) the complete absence of hydrocarbons and organic matter as derived from spectroscopic studies of Venus and (2) the thermodynamic instability of organic compounds particularly in a mildly oxidizing atmosphere."

The question of whether the clouds of Venus are 'smog' or not depends upon how one defines that complicated mixture of substances (which can include ozone, oxides of carbon, nitrogen and sulfur as well as hydrocarbons). The most popular source of 'smog' on Venus is volcanoes (Davidson and Anderson, 1967).

Another interesting suggestion for the composition of the clouds is C₃O₂. It was proposed by Sinton (1953), Kuiper (1957), and Harteck *et al.* (1963). Sinton and Strong (1960) note that "Carbon suboxide is an unstable molecule and readily polymerizes, on standing to a reddish or whitish mass. This polymerization may explain the clouds of Venus." Sagan (1961) raised the objection that carbon suboxide polymers have too low a reflectivity to be the main constituent of the clouds.

Plummer and Carson (1970) have presented convincing evidence that the clouds can not be either C₃O₂ or C₃O₂ polymers, "although very slight traces of low polymer might be present and visible as a yellow stain (in ice clouds, for example) without being otherwise detectable." Although gaseous C₃O₂ has never been observed in any spectra of Venus [upper limits of 5–10 cm atm, 0.5 cm atm, 0.2 cm atm and 0.1 cm atm have been given by Owen (1968a, b), Jenkins *et al.* (1969), Kuiper (1969), and

Plummer and Carson (1970) respectively] it was argued that this was to be expected if only polymers composed the clouds. In their experiments on C_3O_2 , Plummer and Carson found, "Each polymer will continue to polymerize further as long as the ultra-violet light is present. By the time the monomer is exhausted, many of the molecules present are quite heavy, with a deep brown color. We have observed this process. Although polymerization could occur under solar ultraviolet irradiation in the Venus

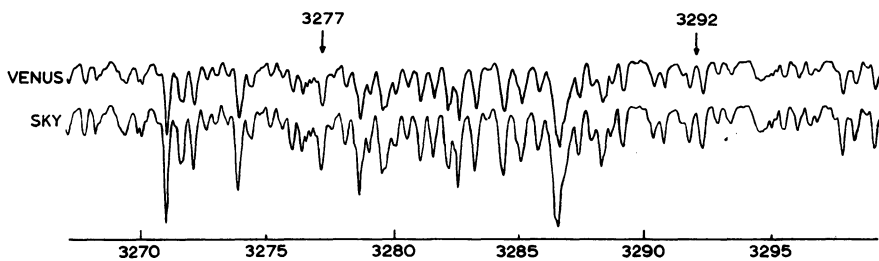


Fig. 7. Spectra of Venus and the sky in the region of carbon suboxide absorption features at 3277 Å and 3292 Å. (From Owen, 1968, *J. Atmospheric Sci.* **25**, 583.)

clouds, we question whether the monomer could be entirely removed in this way without forming more than the slightest trace of heavier molecules which would show intense yellow, red, and brown coloration. Certainly the polymerization would proceed indefinitely, and a continual supply of monomer would have to be invoked to make the clouds perpetually white. We do not believe that the newly formed monomer could escape detection at 2.27μ ." The index of refraction of C_3O_2 is in agreement with that deduced from the polarization data. But the cloud particles would have to have a radius $r < 0.05 \mu$ (in contrast with a radius $r = 1.1 \pm 0.1 \mu$ required by the polarization data) in order to have a reflection spectrum like that observed for Venus.

The detection of HCl in the atmosphere of Venus (Connes *et al.*, 1967) led to the suggestions that the cloud particles could be made of NH_4Cl (Lewis, 1968a, b), aqueous HCl solutions (Lewis, 1968a, b), Hg_2Cl_2 and other compound of Mercury (Lewis, 1969) and incompletely hydrated $FeCl_2$ (Kuiper, 1969). Lewis (1968a, b) showed HCl solutions would evaporate at the temperatures measured for the clouds ($T_c = 235$ K from radiometric observations and $T_c = 250$ K from spectroscopic observations). In order for the clouds to be made of aqueous HCl solutions, they would have to contain about 25% by weight HCl and be at a temperature of 216 K. The discrepancy with the observed temperature led Lewis to conclude "It appears that NH_4Cl must be considered a possible cloud constituent on Venus. Aqueous HCl and solid HCl hydrate clouds, if anywhere present, must be extremely tenuous; pure water and ice seem impossible to reconcile with the best spectroscopic observations." From Table I we see that the refractive index of NH_4Cl is much larger than that required by the polarization measurements, so that it is ruled out as a possible cloud constituent. Lewis (1969) came to a similar conclusion also on the basis of chemical arguments: "Lewis' suggested NH_4Cl should probably be discounted in light of the fact the

proposed condensate would almost certainly lie too deep in the atmosphere to account for the observed temperature of the cloud layer.”

Lewis' suggestion (1969) that “The ‘visible cloud deck’ on Venus, at a temperature near 240K, is composed of a thin haze of Hg_2Cl_2 overlying a deep cloud of liquid Hg droplets” is ruled out by the refractive index data: for Hg_2Cl_2 , $n = 1.97$. Similarly, partially hydrated FeCl_2 , $n \approx 1.55$ does not agree with the polarization measurements.

Although hydrochloric acid clouds are incompatible with the observed temperature at the top of the clouds on Venus, they have been a popular contender for the composition of her clouds. For example, in a review article on the composition of the upper clouds of Venus, Rea (1972) says, “It is concluded that the leading candidate for the uppermost clouds is liquid drops of $\text{HCl-H}_2\text{O}$, that there is no recommended candidate for the second cloud deck, and that H_2O ice is at most a minor component of these cloud systems.” ... “Lewis (1971a, b) has estimated theoretically that the refractive index of such a solution is between 1.42 and 1.43, in reasonable agreement with the polarization results. Moreover such a solution will absorb strongly in the 3–4 μ region because of strong broad bands of the H_3O^+ ion.”

The fact that strongly ionized acids all show the absorption feature near 3 μ characteristic of the H_3O^+ led Young and Young (1973) to examine the spectra of HCl and other acids. While their survey showed the spectrum of Venus was incompatible with the spectrum of aqueous HCl solutions, the spectrum of sulfuric acid was in qualitative agreement. Clouds composed of sulfuric acid have an absorption feature at 11.2 μ which is observed in the spectrum of Venus (Sinton and Strong, 1960; Gillett *et al.*, 1968; Hanel *et al.*, 1968) and has not been identified. Young (1973) has presented some of the arguments in favor of sulfuric acid clouds: the refractive index agrees with the polarization measurements, sulfuric acid is produced photochemically in the Earth's atmosphere, etc. Sill (1973) had postulated sulfuric acid clouds on Venus at an earlier date, employing somewhat different chemical arguments. On the other hand, Lewis (1971a, b) believes that the failure to detect H_2S or COS in the spectrum of Venus argues against the possibility of the clouds being composed of a sulfur compound.

The question of the composition of the clouds does not appear to be closed. Their light yellow color and low albedo in the ultraviolet have not been explained by any of the postulated cloud substances other than hydrated ferrous chloride, which has been ruled out for other reasons.

2. Modern Spectroscopic Observations of Venus

2.1. DISCOVERY OF CARBON DIOXIDE

Although some of the observational methods employed today are very similar to those used by St. John and Nicholson in the 1920's, we have chosen to begin the ‘modern’ era with the discovery of absorption features in the spectrum of Venus.

Adams and Dunham (1932) set out to search once again for the elusive atmospheric O_2 and H_2O in the spectrum of Venus. “Recent progress at the Research Laboratory

of the Eastman Kodak Company in sensitizing photographic plates to the infrared has made it possible to extend this investigation to the region of longer wavelengths where the A band of oxygen at $\lambda 7594$ and the group of strong water-vapor lines in the interval $\lambda 8150$ – $\lambda 8300$ afford excellent material for a sensitive test of molecules of these gases in the atmosphere of Venus." The photographic plates used by St. John and Nicholson (1922) were not sensitive this far out in the infrared and they had been restricted to a part of the spectrum where neither oxygen or water absorbed very strongly. With the possibility of observing Venus in the infrared where the absorption was known to be stronger, Adams and Dunham (1932) stood a much better chance of detecting these molecules in the atmosphere of Venus. They found "no lines of measurable intensity due either to oxygen or to water vapor are present in the spectrum of Venus," but they discovered three bands not appearing in the solar spectrum with heads at $\lambda 7820.2$, $\lambda 7882.9$ and $\lambda 8688.7$. From measurements of the spacing of the lines in these bands and theoretical knowledge of band structure, Adams and Dunham presumed the bands to be due to carbon dioxide. This claim was substantiated by the theoretical work of Adel and Dennison (1933). The carbon dioxide band at 8689 \AA was measured in an absorption cell by Adel and Slipher (1934). They reported, "The lower limit of an estimate on the CO_2 content of the absorbing strata of Venus is apparently two mile atmospheres (3 km atm) whereas the amount actually present in these layers is very probably several times greater ... and this is, presumably, just a very small fraction of the total CO_2 content of the entire atmosphere. In the upper strata alone, Venus possesses 10^4 times as much CO_2 as is present in the entire atmosphere of the Earth."

2.2. OBSERVATIONS IN THE 'FAR' INFRARED

It is relatively recently that spectroscopic observations of the planets began to be made in the 'far' infrared region of the spectrum. Infrared spectra of various gases have been measured in the laboratory since the 19th century. For example, Paschen (1894) recorded the spectra of carbon dioxide and water vapor in the wavelength region 1 to 5μ . Rubens and Aschkinass (1898) measured the spectra of these gases out to a wavelength of 20μ . Ångström (1890) discussed the influence of CO_2 and H_2O absorption features in the solar spectrum on the spectral distribution of solar energy measured at sea level. An extensive catalog of the infrared spectra of various substances was prepared by Coblentz (1905). It must be admitted that these early measurements of infrared spectra were made at comparatively low resolution because the detectors were none too sensitive. For laboratory measurements, it was possible to obtain bright light sources and there was little restriction on the length of time available to make the measurement of the spectrum. The lack of sensitive detectors prevented many astronomical observations from being made in the 'far', i.e. non-photographic, infrared for a number of years.

As one might expect, the Sun was the first astronomical object to have its spectrum measured. Most of the strong absorption features in the infrared solar spectrum are due to molecules in the Earth's atmosphere. Lemansky (1871) used a thermopile to

measure the energy in the solar prismatic spectrum and attributed the three absorption features which he recorded to the Earth's atmosphere. The first systematic analysis of the near infrared solar spectrum was begun by Langley in 1881 and completed in 1900 (Langley and Abbot, 1900). The solar spectrum was measured between 0.8 and 5 μ . Adel *et al.* (1935) extended the spectral coverage from 5 to 21 μ .

Kuiper (1947) was the first to measure the spectrum of Venus in the 'far' infrared. Kuiper was able to make measurements beyond 2 microns and his early spectra revealed 'nine strong CO₂ bands'. The McDonald Observatory report (Struve, 1948) notes that "Herzberg is engaged in the study of CO₂ with the long absorption tube. The bands found by Adams and Dunham as well as the new bands reported last year, in Venus, have been reproduced in the laboratory with appropriate pressures. The amount of CO₂ above the reflecting layer of Venus corresponds to at least 2200 m at atmospheric pressure. Since the intensity distribution within the bands, as photographed in the tube is similar to that observed in Venus, the appropriate layer in the atmosphere of Venus has about room temperature."

Kuiper (1949) continued his pioneering observations of Venus in the infrared, at McDonald Observatory, and found many more carbon dioxide bands in his spectra. He discovered the systematic variation in the CO₂ absorption band at 8689 Å; it is weakest near inferior conjunction ($i = 180^\circ$) and increases in strength by almost a factor of 10 near superior conjunction ($i = 0^\circ$). Kuiper (1952) also reported "that day-to-day fluctuations of considerable magnitude occur and that the observed distribution of CO₂ is often remarkably patchy over the disc. The patches are of such a size that they may correspond to the cloud features shown on ultraviolet photographs."

"Evidently, the Venus cloud layer is in violent motion ... It is recalled that the radiometric measures by Pettit and Nicholson have shown the dark side of Venus to emit nearly as much infrared radiation as the sunlit side, which also points to a vigorous convection in the Venus atmosphere."

2.3. THE SEARCH FOR MINOR CONSTITUENTS IN THE ATMOSPHERE

Kozyrev (1954a, b, 1969) reported on two emission features which showed up in the violet region of the spectrum of Venus and also in the spectrum of smoke from volcanic eruptions. Warner (1960) suggested that some of the features noticed by Kozyrev occurred at the same wavelengths as known bands of N₂, N₂⁺, O and O⁺ and could be due to these species. However Newkirk (1959), Heyden *et al.* (1959), Richardson (1960), Spinrad (1962a-e), and Owen (1968a, b) searched for the emission features in their spectra of Venus and failed to find them. Spectroscopic searches for O₂ and oxides of nitrogen on Venus have proven fruitless which suggests that Warner's proposed identification of the Kozyrev bands may have little to do with the atmosphere of Venus. The bands are certainly seldom present in the spectrum of Venus and are possibly spurious.

Kuiper (1952) reported an upper limit of 100 cm atm for N₂O based on his infrared spectra. The NO₂ molecule absorbs in the visible region of the spectrum but these bands (Herzberg, 1966) have not been observed in the spectrum of Venus.

2.4. SCATTERING IN THE ATMOSPHERE OF VENUS

The next report on the spectrum of Venus (Chamberlain and Kuiper, 1956) had to do with the determination of the rotational temperature of a carbon dioxide band. Earlier estimates of the 'cloud-top' temperature had been based on visual comparisons of the Venus spectrum with laboratory spectra of carbon dioxide (Adel, 1937; Herzberg, 1951). Dunham (1949) had measured the intensities of the CO₂ lines in the Venus spectra photographed at Mt. Wilson Observatory and had estimated that the temperature was $T = 300 \pm 50$ K. Chamberlain and Kuiper (1956) say, "In these earlier estimates it was assumed in all cases that the relative intensities of the lines were proportional to the relative populations, N_j , of the lower levels of the transition. Van de Hulst (1952, p. 102) has pointed out, however, that in an optically thick atmosphere, where scattering and absorption are both important, this simple relation would not be expected to hold true. In particular, for an optically thick planetary atmosphere scattering light isotropically, the line absorption for weak lines is proportional to $(N_j)^{1/2}$." This was the first suggestion that the interpretation of the CO₂ absorption bands in the spectrum of Venus, could be much more complicated than their interpretation in laboratory spectra. Of course, the presence of clouds on Venus was well known, but here-to-fore it had generally been assumed that the measured absorption referred to the amount of gas above the clouds; the clouds on Venus had been regarded as quite dense, so that most of the absorption occurred above the cloud deck and the infrared radiation did not penetrate very far into the clouds themselves.

On the basis of their square-root absorption law, and a slightly faulty relationship between the equivalent width and the intensity of rotational lines, Chamberlain and Kuiper (1956) found a mean temperature of $T_{\text{rot}} = 285 \pm 9$ K (p.e.). They remarked that "The most important systematic errors in T_{rot} probably arise from our neglect of the variation of oscillator strength with the different lines in a band and from departures of the absorption law from the asymptotic relation" $W(J) = \text{const } (N_j)^{1/2}$. Chamberlain (1965) subsequently estimated that use of the correct expression for the oscillator strength (or line intensity) "would lower all 'radiative transfer' values of T_{rot} by about 7% or 20 K. The correction to the 'simple reflection' values of T_{rot} would be about twice as great."

It was assumed, at that time, that any interpretation of a spectrum which postulated the clouds acted as a reflecting layer would have the absorption linearly proportional to the number density of absorbing molecules. That is, the equivalent width of a line, $W(J)$, was equal to the product of the line intensity $S(J)$ and the amount of absorbing gas, w :

$$W(J) = S(J) w. \quad (1)$$

It was well known from laboratory studies that this relation only held in certain situations. If the pressure, for line formation, is high enough that Doppler broadening can be neglected, then the lines are broadened by intermolecular collisions and have a

dispersion line contour or Lorentz line shape. The spectral absorption coefficient of the line, $\kappa_\omega(J)$, is given by

$$\kappa_\omega(J) = [S(J) \gamma(J)/\pi] [(\omega - \omega_J)^2 + \gamma(J)^2]^{-1}, \tag{2}$$

where ω_J is the frequency (or wavenumber) of the center and $\gamma(J)$ is the halfwidth of the line at half of its maximum depth. Ladenburg and Reiche (1913) showed that the equivalent width of a Lorentz line is given by two asymptotic relations:

$$W(J) \simeq S(J) w \quad \text{for } x(J) < 2/\pi \tag{3a}$$

and

$$W(J) \simeq 2[S(J) \gamma(J)w]^{1/2} \quad \text{for } x(J) > 2/\pi, \tag{3b}$$

where

$$x(J) = [S(J)w/2\pi \gamma(J)].$$

The line intensity $S(J)$ is directly proportional to the number of molecules per unit volume, N_J , times the oscillator strength, and the line halfwidth $\gamma(J)$ is directly proportional to the total pressure. Depending on the pressure for line formation, absorption lines can follow either a linear or a square root absorption law *in the absence of scattering*.

This fact was largely ignored in the early interpretation of Venus spectra and has caused a certain amount of confusion in the literature. The idea that scattering particles would increase the effective absorption path in the atmosphere of Venus was sufficiently novel that some people assumed that the old laws of gaseous absorption no longer applied. A new brand of physics was needed to interpret the observations. Radiative transfer theory was called into play. Without going into all the mathematical details (which are sufficiently complicated that the physical processes involved are sometimes forgotten!) we will briefly summarize the situation. The transfer equation involves I_ω the radiant flux in the frequency interval between ω and $\omega + d\omega$ per unit projected area per unit solid angle; I_ω is termed the (spectral) intensity of radiation. (Note that this is a different use of the word intensity than is meant by the intensity, or strength, of a spectral line). The change in radiation intensity in the direction S is given by

$$\frac{dI_\omega}{ds} = -(\kappa_\omega + \sigma_\omega) I_\omega + \kappa_\omega B_\omega + \sigma_\omega \int I_\omega \frac{d\Omega}{4\pi}. \tag{4}$$

Here σ_ω is the (spectral) scattering coefficient, B_ω is the Planck function, and Ω is the solid angle. For a plane-parallel atmosphere it is customary to use the geometrical depth measured from the top of the atmosphere,

$$dz = - ds \cos \theta,$$

where θ is the direction of radiation measured from the outward normal to the atmosphere, and to introduce the variables $\mu = \cos \theta$, the optical depth τ ,

$$d\tau = (\kappa_\omega + \tau_\omega) dz$$

and the dimensionless quantity $\tilde{\omega} = \sigma\omega(\kappa_\omega + \sigma_\omega)^{-1}$. Then (4) can be written as

$$\mu \frac{dI_\omega}{d\tau} = I_\omega + (\tilde{\omega} - 1) R_\omega - \tilde{\omega} \int I_\omega \frac{d\Omega}{4\pi}. \quad (5)$$

For isotropic scattering, the flux integral in (5) reduces to

$$\int I_\omega \frac{d\Omega}{4\pi} = \frac{1}{2} \int I_\omega d\mu, \quad (6)$$

(but what real cloud behaves as an isotropic scatterer?). The basic idea of the Milne-Eddington approximation (Kourganoff, 1952) is to assume that the angular dependence of the intensity, I_ω , can be expressed in terms of a series of Legendre polynomials, $P_l(\mu)$. These form a complete set of orthogonal functions in the interval $(-1, 1)$, which is just the interval through which μ varies. The reason for doing this is to obtain closed-form solutions to the equation of transfer in terms of functions that are well known. There is a problem with this approach, however. The function I_ω is discontinuous and trying to represent it by a *finite* sum of Legendre polynomials is clearly impossible. Chandrasekhar (1950) tried to get away from the difficulty by introducing the method of discrete ordinates. He chose to fix the determination of $I_\omega(\tau, \mu)$, at the optical depth τ , to $2n$ points corresponding to $2n$ discrete values of μ_i which are more or less regularly distributed in the interval $-1 < \mu < 1$. This results in $2n$ linear differential equations for the $2n$ unknown functions $I_\omega(\tau, \mu_i)$. These can be integrated and the constants of integration are found from the boundary conditions.

The observational data of Kuiper had shown that the equivalent width of absorption lines decreased as the Venus phase angle increased. In order to give a theoretical explanation to this effect, which is contrary to what would be expected for a reflecting cloud layer, Chamberlain and Kuiper (1956) utilized a solution to the equation of transfer obtained by Chandrasekhar (1950). This solution referred to a homogeneous planeparallel atmosphere which scattered radiation isotropically and had an albedo for single scattering $\tilde{\omega} < 1$. The intensity for diffuse reflection was given by (Chandrasekhar, 1950; p. 85) as

$$I(0, \mu) = \frac{1}{4} \omega F \frac{\mu_0}{\mu + \mu_0} H(\mu) H(0), \quad (7)$$

where F is related to the net flux of radiation by

$$\pi F = \int I \cos \theta d\Omega.$$

The H -functions had been studied by Chandrasekhar. They are continuous functions which increase monotonically from $H(\tilde{\omega}, 0) = 1$ to $H(\tilde{\omega}, 1) \approx 3$. For isotropic scattering,

$$\int_0^1 H(\tilde{\omega}, \mu) d\mu = \frac{2}{\tilde{\omega}} [1 - (1 - \tilde{\omega})^{1/2}],$$

and for $\tilde{\omega} \sim 1$ there is an asymptotic relation (van de Hulst, 1952, p. 102)

$$H(\tilde{\omega}, \mu) \approx \frac{H(1, \mu)}{1 + \mu [3(1 - \tilde{\omega})]^{1/2}} \tag{8}$$

Chamberlain and Kuiper used (7) and (8) to obtain the following relation for the absorption of a spectral line relative to the continuum ($\tilde{\omega}_c = 1$):

$$A = \frac{I_c - I}{I_c} = \left[1 - \tilde{\omega} \frac{H(\tilde{\omega}, \mu) H(\omega, \mu_0)}{H(1, \mu) H(1, \mu_0)} \right] \tag{9a}$$

or

$$A \simeq (\mu + \mu_0) [3(1 - \tilde{\omega})]^{1/2} = (\mu + \mu_0) [3\kappa/\sigma]^{1/2} \tag{9b}$$

This is how they arrived at the relation that the absorption in a scattering atmosphere should depend on the square root of the line intensity (or absorption coefficient). Chamberlain (1965) then considered the case where the continuum albedo differed from unity. This resulted in the following expression for the line absorption:

$$A \simeq 3^{1/2} (\mu + \mu_0) [(1 - \tilde{\omega})^{1/2} - (1 - \tilde{\omega}_c)^{1/2}] \tag{9c}$$

He noted that “. . . so long as the continuous absorption (κ_c) is less than that due to the gas alone (κ) (i.e. when $1 - \tilde{\omega}_c < \tilde{\omega}_c - \tilde{\omega}$), we may neglect $1 - \tilde{\omega}_c$ with little error. But when the inequality becomes reversed far out in the wings (of a line), the term in square brackets in (9c) rapidly diminishes.” McClatchey (1967) showed that when the line absorption coefficient κ is much smaller than the continuous absorption κ_c the line absorption is given by

$$A \simeq 3^{1/2} (\mu + \mu_0) \frac{\kappa}{2\kappa_c} \left(\frac{\kappa_c}{\sigma} \right)^{1/2} \tag{9d}$$

McClatchey remarked, “Equation (9d) indicates that the absorption is a linear function of the absorption cross-section when $\kappa \ll \kappa_c$. This inequality means that the absorption in the line is much less than that due to the continuous absorption – a situation always realizable in practice for the weakest lines.” The inequality of (9b) where $\kappa_c \ll \kappa$ “on the other hand can only be valid in the case of weak absorption lines when κ_c is itself a very small number. In the limit of weak lines (i.e. $\kappa \rightarrow 0$) we must have $\kappa_c \rightarrow 0$. But $\kappa_c \rightarrow 0$ means that $\tilde{\omega}_c \rightarrow 1$.” McClatchey concluded: “. . . in the physically realistic case of $\tilde{\omega}_c < 1$, the square-root dependence on the absorption cross-section is not an asymptotic limit but rather a cloudy transition region. . . even though the absorption at the line center might correspond to a portion of the curve where it deviates from linearity (say $A = 0.30$), the equivalent widths of the lines would be expected to depart only very slightly from a linear law because most of the area under the absorption curve would result from absorption in the line wings where the monochromatic absorption does follow the linear law. Under this circumstance, it would

seem most accidental if the equivalent widths of weak absorption lines in a scattering and absorbing atmosphere fell on the square root portion of a curve of growth.”

The discussion of the absorption law (or laws) for line formation in cloudy atmospheres has continued up to the present date and we shall return to it later.

2.5. MORE OBSERVATIONS IN THE ‘FAR’ INFRARED

Reports of spectroscopic studies of Venus continued to be rare in the astrophysical literature. Four years after the publication of Kuiper’s observations in the photographic infrared (Chamberlain and Kuiper, 1956), Sinton and Strong (1960) presented the results of their spectroscopic study, made in 1953 and 1954, of Venus at longer

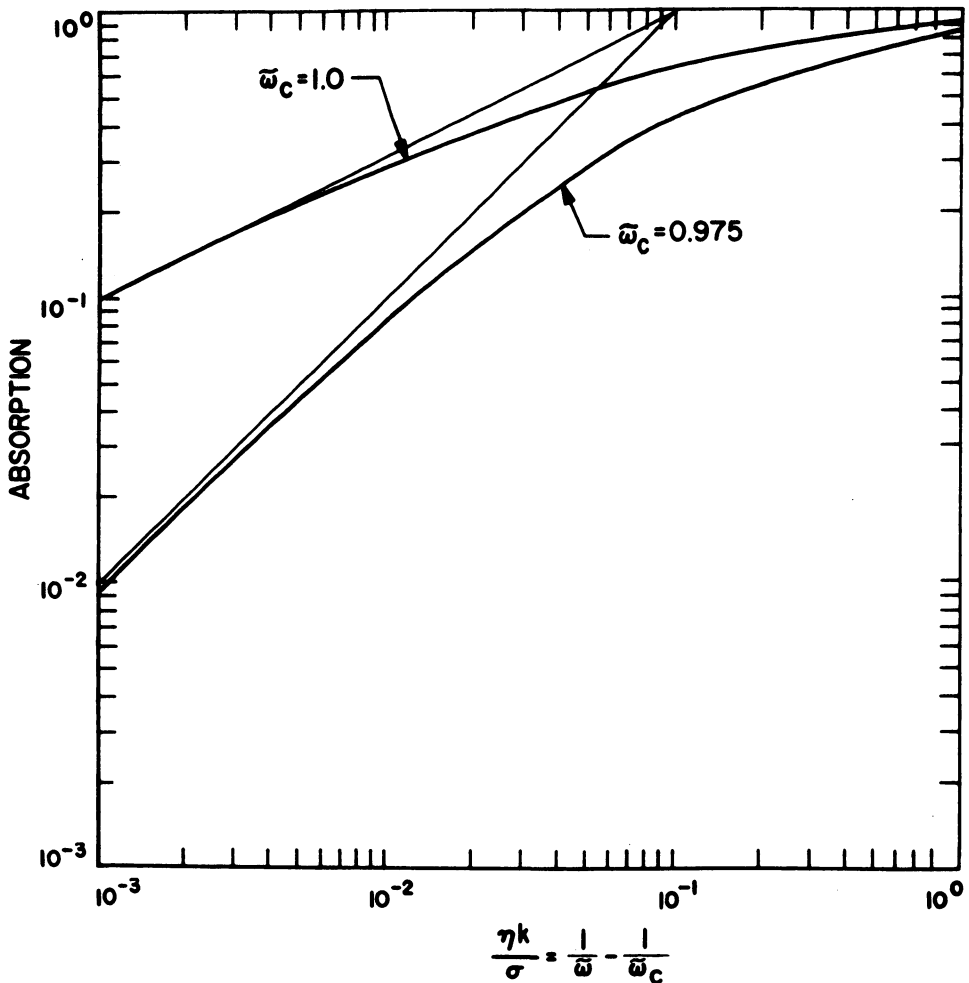


Fig. 8. Curves of growth for monochromatic absorption in a scattering atmosphere. The square-root asymptotic limit is shown for the continuum albedo equal to 1.0; the linear asymptotic limit is shown for the continuum albedo equal to 0.975. (From McClatchey, 1967, *Astrophys. J.* **148**, L93.)

wavelengths, between 8 and 13 μ . Sinton and Strong remarked that "Prior to obtaining these spectra it was expected that we would find the absorption bands of carbon dioxide at 9.4, 10.4 and 12.6 μ very intense in the spectrum of Venus. ... The spectrum shows no evidence for the 9.4 and 12.6 μ bands and the depression at 11 μ extends to too long a wavelength to be associated entirely with the band at 10.4 μ A diffuse band at 11.2 μ was found in the spectrum of Venus in addition to a carbon dioxide

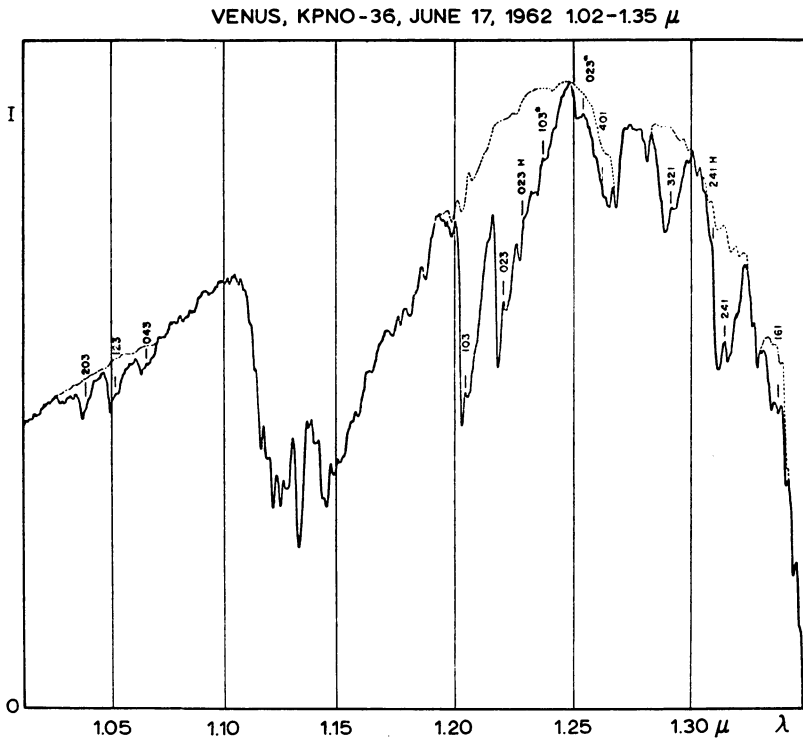


Fig. 9. Spectrum of Venus between 1.02 and 1.35 μ . The dashed upper curve shows the solar comparison spectrum, where it is different from the Venus spectrum. Carbon dioxide bands are identified by the quantum numbers of the upper state; an *H* indicates a 'hot' band; the C^{18} isotopic bands are indicated by an asterisk. (From Kuiper, 1962, *Comm. Lunar Planet. Lab.*, No. 15.)

band at 10.4 μ . The 10.4 band was found much weaker than expected." Their failure to observe some of the expected CO_2 bands let Sinton and Strong to postulate "That the radiation is being absorbed by a gray material above most of the CO_2 . The low radiometric temperature compared with the higher temperature corresponding to the top of the cloud level obtained by Chamberlain and Kuiper (1956) and earlier by Adel (1937), also indicates that the radiating level is above the cloud top. ... The absorption may not really be gray but may be due to gases that just fill in the absorption around the CO_2 bands and perhaps have somewhat stronger absorption at 11.2 μ ."

The first comprehensive study of the infrared spectrum of Venus was published by Kuiper (1962). It covered the spectral region 1.0–2.5 μ . Kuiper noted that “The Venus spectra give information on (a) the CO_2 abundance on Venus; (b) the $^{13}\text{C}/^{12}\text{C}$ ratio; (c) the $^{18}\text{O}/^{16}\text{O}$ ratio; (d) the hot bands.” Kuiper found an abundance of “about 2 km atm of CO_2 However, since the strength of the CO_2 absorption on Venus is variable, both with the phase and from day-to-day, and even region to region on the planet (Kuiper, 1952), the amount of CO_2 found only applies to the date of observation.” The isotope ratios $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ were “equal to that on the Earth

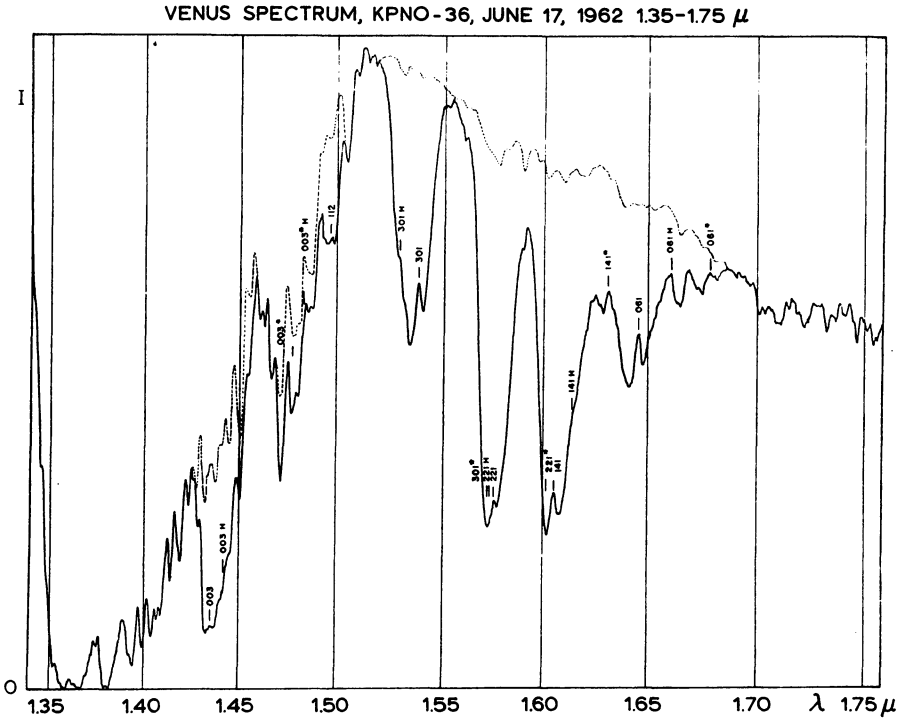


Fig. 10. Spectrum of Venus between 1.35 and 1.76 μ . (From Kuiper, 1962, *Comm. Lunar Planet. Lab.*, No. 15.)

within the error of measurement” which Kuiper estimated to have a precision of $\pm 10\%$. So-called ‘hot’ bands are those whose lower vibrational state is an excited one, rather than the ground state. As the temperature in the laboratory is increased above room temperature, the population of the excited vibrational states is increased relative to the ground state. This causes the intensity of the ‘hot’ bands to be enhanced and the intensity of the ground state bands to be diminished. As a result, the hotter the gas becomes, the more the absorption due to the hot bands increases and they appear much more prominently in the spectrum than they do at room temperature. Kuiper’s (1962) measurements of the CO_2 hot bands suggested “that the Venus temperature is considerably higher than the laboratory temperature.” Subsequent measurements made

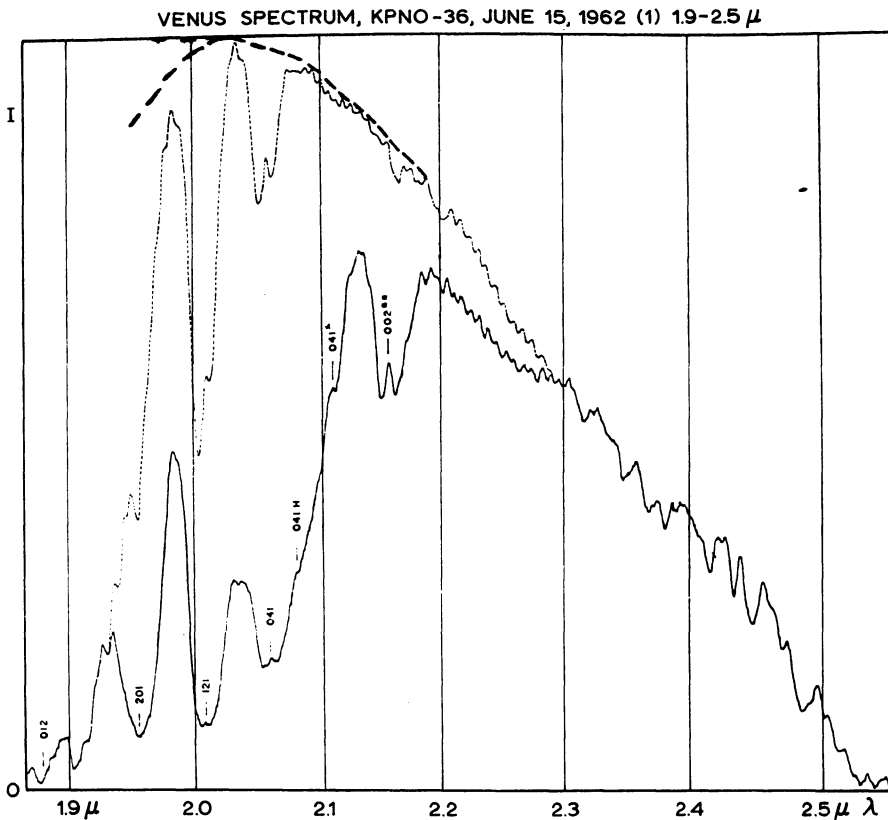


Fig. 11. Spectrum of Venus between 1.9 and 2.6 μ . The solar comparison spectrum is indicated and an estimate of the solar continuum is also shown. (From Kuiper, 1962, *Comm. Lunar Planet. Lab.*, No. 15.)

at higher resolution (Connes *et al.*, 1967) failed to confirm this suggestion when they revealed that the hot bands were in many cases blended with isotopic CO_2 bands. The blending results in an over-estimate of the equivalent width of the hot bands and hence an over-estimate of the temperature. Kuiper was unable to detect the carbon monoxide band at $\lambda 2.35 \mu$ and reported an “upper limit of 10 cm atm_{stp}”, implying an approximate upper limit of one-fourth of this amount for a vertical column in the Venus atmosphere” (or a mixing ratio of less than 50 parts per million).

2.6. SIMPLE INTERPRETATIONS OF THE SPECTRUM OF VENUS

There was one peculiarity about the spectrum of Venus that was particularly troublesome. Herzberg (1951) had reported that the strong bands near 1.6μ are roughly matched by 88 m atm of CO_2 at a pressure of 1 atm in the laboratory but more than 1400 m atm of CO_2 were needed to match the weaker bands near 1.05μ . Kaplan (1961) believed this discrepancy was “mostly due to the fact that the laboratory measurements were made at 1 atm, which is an order of magnitude higher than the

mean pressures we will later derive for the atmosphere above the reflecting layer." Kaplan assumed that the individual lines in the 1.6μ absorption band followed a square-root absorption law and that the overlapping of adjacent lines was small. This meant that the absorption by the entire band should follow a square-root absorption law. Kaplan found that the laboratory measurements of Howard *et al.* (1951) of the CO_2 band at 1.6μ could be fit by

$$W = 8.4 [(wp) (1 + 0.3f)]^{1/2}, \quad (10a)$$

where W is the equivalent width of the band, in cm^{-1} ; w is the amount of CO_2 , in m atm; p is the pressure, in atm, and f is the fraction of CO_2 by volume. For a uniformly mixed gas in a planetary atmosphere the appropriate pressure is one half that at the reflecting layer ($p = p_r/2$) and the absorption path length $w = 2u \sec \theta$, where u is the amount in a vertical column. Thus (10a) became for Venus

$$W = 8.4 [up_r \sec \theta (1 + 0.3f)]^{1/2}. \quad (10b)$$

Kuiper's (1947) observations indicated that the equivalent width of the 1.6μ band was at least as large as $W = 150 \text{ cm}^{-1}$. Assuming $\sec \theta = 2$, Kaplan (1961) found

$$up_r = \frac{(150)^2}{2(8.4)^2 (1 + 0.3f)} = \frac{159}{1 + 0.3f}.$$

Assuming the atmosphere of Venus was composed of pure CO_2 ($f = 1$), then the amount of CO_2 can be related to the cloud top pressure by $u = 5.93 \times 10^3 p_r$ meters. This gave Kaplan a lower limit to the reflecting layer pressure of $p_r \geq 0.14$ atm (or 140 mb and $u \leq 830$ m). Kaplan argued that the temperature of 235 K measured by Sinton and Strong (1960) is "a reasonable value for the cloud-top temperature." He used the temperature of 285 K reported by Chamberlain and Kuiper (1956) as the "temperature at a level having half the pressure of the effective reflecting surface." Assuming an adiabatic lapse rate between the reflecting surface and the cloud top, Kaplan concluded "the pressure at the cloud top will be about one-fourth of p_r ." Kaplan then went on to find the mixing ratio of CO_2 and the surface pressure. He used the then current microwave measurements of 585 K for the surface temperature and de Vaucouleurs and Menzel (1960) measurements of the occultation of Regulus. These data plus 'a reasonable guess' led Kaplan to conclude that the cloud top pressure is "about 90 mb", the CO_2 concentration is "about 15% by volume", "the surface pressure is of the order of two atmospheres and the total CO_2 (is) of the order of 2 km atm_{sp}." While Kaplan's conclusions based on other data have subsequently proved to be faulty, the results of his interpretation of the spectra are not all that different from current results.

The first attempt to seek observational evidence as to whether the clouds of Venus behaved as a scattering haze or as a reflecting layer was made by Spinrad (1962a). His investigation "was originally motivated by interest in a possible variation of the CO_2 rotational temperature with Venus phase." To do this, Spinrad used "the ten best old Mt. Wilson 100-in. coudé spectrograms of Venus" taken by Adams and Dunham in

the 1930's; the plates covered Venus phase angles from 51° to 113°. Spinrad found rotational temperatures for the CO₂ band at 7820 Å in two ways: first, he used “the ordinary Boltzmann equation method with the assumption of W being directly proportional to $N(J)$, (which is) obviously true for weak lines”; second, he used “a radiative transfer scheme of Chamberlain and Kuiper where $W \sim [N(J)]^{1/2}$.” Spinrad also made the faulty assumption of “equal oscillator strengths for all the J lines.” For the linear absorption law, Spinrad obtained rotational temperatures ranging from 214 K to 445 K. For the square-root absorption law, he found temperatures ranging from 142 K to 433 K. Spinrad noted that, “In general the rotational temperatures given by the usual application of the Boltzmann equation are somewhat higher than those derived with the radiative transfer modification. ... If a choice of (models for) rotational temperatures is to be made at this time, the decision must be made on rather arbitrary empirical grounds. We shall reject the method which gives rotational temperatures far different from any other temperatures found for Venus by other means.” Since the highest temperatures Spinrad had found from both of the two absorption laws were considerably colder than the microwave results for the ‘surface temperature’ (of ~600 K), he chose to reject the absorption law which yielded temperatures lower than the coldest reported ‘measurement’ of temperature. Menzel and de Vaucouleurs (1960) had derived a temperature of $T = 210$ K from their occultation data, based on the assumption that the atmosphere of Venus consisted solely of N₂. Spinrad argued that “The radiation transfer rotational temperatures... fall well below 210 K on two occasions, so on these grounds of incompatibility we shall rule against the Chamberlain-Kuiper method... .” Spinrad estimated that “both systematic and internal errors in the rotational temperatures... are probably smaller than ± 50 K... .”

He remarked, “One more very crucial point remains to be mentioned. The Venus CO₂ lines are lines whose total absorption is integrated over (an atmospheric) region with a rather large temperature gradient... Each line will be partially weighted by the high, cool carbon dioxide gas and also by the lower, hotter layers of the Venus atmosphere... The effect is to make the rotational temperature an average quantity which applies directly to some unknown, but intermediate level in the CO₂ absorbing region.”

Spinrad next attempted to determine the pressure where the lines were formed. Making the usual kinetic theory assumption about the dependence of the line half-width γ on temperature and pressure,

$$\gamma = \gamma^\circ (p/p_0) (T_0/T)^{1/2}, \quad (11)$$

Spinrad used the value of γ° appropriate for nitrogen-broadened CO₂ lines. This was because “Kaplan (1961) finds the CO₂/N₂ mixing ratio to be about 0.2.” Spinrad measured the apparent halfwidths of the CO₂ lines on the ten Mt. Wilson spectrograms. He made corrections “for the finite slit-widths of the spectrograph and microphotometer... The largest corrections to the halfwidths were about 15%.” Young and Young (1972) have suggested that Spinrad’s failure to also correct for the point-spread function of the photographic plates led him to believe that the apparent halfwidths were quite similar to the true halfwidths.

Spinrad's familiarity with stellar spectra had caused him to make two assumptions which are valid for stellar spectra and very dangerous for planetary spectra: Stellar lines tend to be fairly broad and have a comparatively large halfwidth, hence the observed line profile is fairly close to the true line profile; in the planetary case, the lines are usually much narrower than the spectral slit width and the observed line profile is more likely to resemble the slit function than the true line shape. Secondly, a stellar line with an equivalent width of 25–100 mÅ will have an absorption that varies linearly with the amount of gas over the entire line profile; a planetary line of the same equivalent width may be strongly saturated (i.e. the absorption may increase with the amount of gas at a much slower rate than a linear one), near the center of the line profile. As a result, the halfwidth of the actual absorption line profile $A_\omega = 1 - \exp(-\kappa_\omega \omega)$ (measured as the width of the line at half the maximum absorption depth) may be much larger than the halfwidth of the absorption coefficient, κ_ω .

Spinrad reported, "the pressure at the bottom of the Venus CO₂ path averages about 7 atm, but may occasionally reach 10 atm." He also found "Venus to have about 2 km atm of carbon dioxide" in the absorption path. "The partial pressure of 2 km atm of CO₂ is $\frac{1}{3}$ atm. The average total pressure down to the bottom of the CO₂ absorbing layer is about 7 atm. Thus the CO₂ abundance by mass, and presumably the CO₂/N₂ mixing ratio is about 5%. This estimate is uncertain by a factor of 2. Carbon dioxide appears to really be only a minor constituent of the Cytherian atmosphere."

Prior to the papers of Kaplan and Spinrad, carbon dioxide has appeared to be the major atmospheric constituent (since it was the only molecule that has been definitely

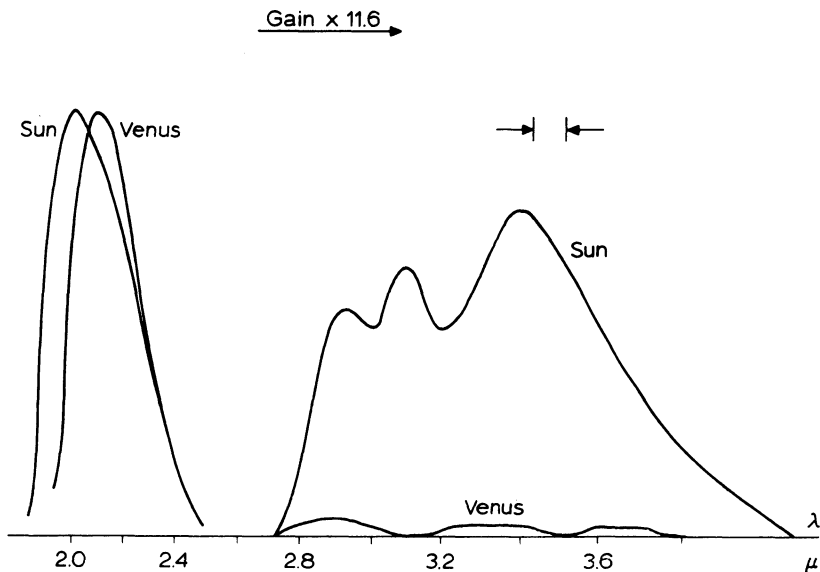


Fig. 12. Prism spectrum of Venus between 2.0 and 3.8 μ . (From Moroz, 1964b, *Mem. Soc. Roy. Sci. Liège* 9, 406.)

detected on Venus). When CO₂ was 'shown' to be a minor constituent, the possibility that the atmosphere of Venus was similar to that of the Earth was revived, if only O₂ or water vapor could be detected.

2.7. THE SEARCH FOR H₂O AND OTHER CONSTITUENTS IN THE ATMOSPHERE OF VENUS

In another effort to detect H₂O lines on Venus by the Doppler shift method, Spinrad (1962b, c) selected "an excellent old high-dispersion spectrogram of Venus taken by Adams and Dunham at the 100-in. coudé focus;" the spectrogram was taken when the Venus lines would be Doppler shifted -0.37 \AA from the telluric water lines, at 8180 \AA . From his analysis of the CO₂ band at 7820 \AA on this same plate, Spinrad found that it "refers to a region deep in the Venus atmosphere. This would tend to maximize the possibility of detecting any Cytherian H₂O lines. The rotational temperature of the $\lambda 7820 \text{ CO}_2$ band is $T_{\text{rot}} = 440 \text{ K}$ (Spinrad, 1962a) and the average pressure in the CO₂ absorbing layer is about 4 atm. ... Presumably, any very weak hypothetical Venus H₂O lines would also originate at a deep atmospheric level."

Adams and Dunham had taken the Venus plate on 23 March 1940. No Doppler-shifted H₂O line due to Venus could be detected. Spinrad estimated that the upper limit on any Cytherian H₂O component corresponded to only one part in fifty of the number of molecules producing the telluric H₂O line. Using "the Weather Bureau upper air data for their San Diego station indicates 7 mm precipitable H₂O above 5000 ft on that date. Since the Venus spectrogram was taken at $\bar{z} = 2$, we find the telluric H₂O lines on this plate were produced by 1.4 gm cm^{-2} ." The old Mt. Wilson plate had been taken on a very wet day! Spinrad assumed "the solar radiation path equals about 4 thicknesses of the Venus atmosphere. Thus, the upper limit to the Venus water vapor content is really $(1/50) \times (1/4) = (1/200)$ that over Mt. Wilson or $7 \times 10^{-3} \text{ gm cm}^{-2}$ (70μ)." Since Spinrad had found a base pressure of 8 atm or 8000 gm cm^{-2} from his analysis of the CO₂ lines, he estimated the mixing ratio of water might be less than 9×10^{-7} by mass. He concluded "water vapor is extremely difficult to detect in the Cytherian atmosphere at least down to a region where P is 8 atm."

Spinrad (1962b) also "made a careful search of the near ultraviolet and part of the blue region of the Cytherian spectrum ... Venus shows only the solar reflection spectrum ... The present philosophy of 'groping in the dark' for spectroscopic evidence of absorbers other than CO and CO₂ in the Venus atmosphere seems a painstaking but necessary task. The work will continue."

Spinrad's detailed examination of the Venus spectrograms in the Mt. Wilson Observatory plate files only revealed one new absorption feature: a carbon dioxide band with a head at 7158 \AA (Spinrad, 1962c). Once again, the old Mt. Wilson plates indicated the presence only of CO₂ in the atmosphere of Venus.

Kaplan (1962) examined some of the microdensitometer tracings that Spinrad had made of the Venus plates taken by Adams and Dunham. He suggested that they showed two intensity maxima in the P branch: one corresponding to an effective temperature of 300 K and the other to an effective temperature of 700 K. "The obvious cause of the double maxima is a cloud layer at some level whose temperature is consider-

ably in excess of 300 K, say at 350 to 400 K. ... The cloud, and the gas from which it presumably condenses, are of considerable importance in providing part of the greenhouse effect that is necessary to maintain surface temperatures in excess of 700 K." Supposedly, some of the sunlight was being reflected from the surface of Venus while the rest was reflected by her clouds. Young and Young (1972) showed that it was theoretically impossible to achieve a double maximum in the P branch of a CO_2 band for two *isothermal* layers of the gas unless the temperature ratio of the two layers exceeds ~ 9 . In a planetary atmosphere, with a continuous variation in the temperature between the planet's surface and the top of the atmosphere, the appearance of a double maximum would be very unlikely. Young and Young made statistical tests on the data for which Kaplan had reported two maxima and concluded, "The 'double maximum' phenomenon appears to be exclusively associated with data having a relatively poor signal to noise ratio ... The effect reported by Kaplan was due to noise, and ... it is impossible to detect temperatures as high as 700 K in the atmosphere of Venus by means of ground-based observations of the 7820 \AA CO_2 band."

Dollfus (1963a, b) reported an apparent detection of water vapor in the atmosphere of Venus on 21 January 1963, "Les comparaisons photométriques de la bande 1.4μ de la vapeur d'eau sur Vénus et la Lune en haute montagne en hiver révèlent au moins $10^{-2} \text{ g cm}^{-2}$ de vapeur d'eau au-dessus de la couche nuageuse élevée de Vénus. Les voiles nuageux peuvent donc être de la glace ou de l'eau". Kuiper and Forbes (1967) suggested that "The Dollfus result might be due to residual CO_2 absorption entering his 1.4μ filter." Dollfus had found 280μ of precipitable water in the total absorption path for Venus; using an air mass of 4, this corresponded to 70μ in the vertical path.

Sinton (1962a, b, 1963, 1964a, b) reported "Spectra of Venus that were obtained at Lowell Observatory gave an indication that CO was present in this planet's atmosphere although the band was rather weak. This question is still not resolved because the shape of the observed band indicates that the CO is at a considerably lower temperature (80 K) than most people would assume is present – even high in the Venus atmosphere." The distortion in the shape of the CO band in the Venus spectra was due to unresolved blends in these spectra. The observations of Connes *et al.* (1968) at much higher resolution than Sinton's measurements revealed no peculiarities in the contour of the band; "Analysis of the lines of the principal isotopes shows that they are formed at cloud level, with an effective temperature of 240 K and a total effective CO path of 13 cm amagat. Comparison with CO_2 lines yields a CO/ CO_2 ratio of 45 parts per million."

In 1962 and 1963, Moroz (1964a, b) measured the infrared spectra of Venus using the 50-in. reflector of the South Station of the Astronomical Institute in Crimea. Moroz also reported the detection of carbon monoxide (at 2.35μ) in his spectra: "This depression is equivalent to approximately 4 cm atm in the laboratory spectra. Consequently, the CO abundance in a vertical column of the atmosphere of Venus above the cloud layer must be about 1.5 cm." Moroz (1964a, b) remarked that "The intensity of Venus in the region 3.5μ was found still lower than in Sinton's (1961) previous observations. The minima at 3.18 and 3.57μ seem to be real... A constituent, which

produces this absorption is still unidentified (it is not H_2O), but is of great importance to the physics of Venus. As it absorbs the solar radiation, it absorbs also an intrinsic radiation of the planet. It must create great greenhouse effect, heating the planetary surface to a high temperature..." The absorption features in the neighborhood of 3.5μ may be due to the clouds. Because of the low intensity of the Venus spectrum in

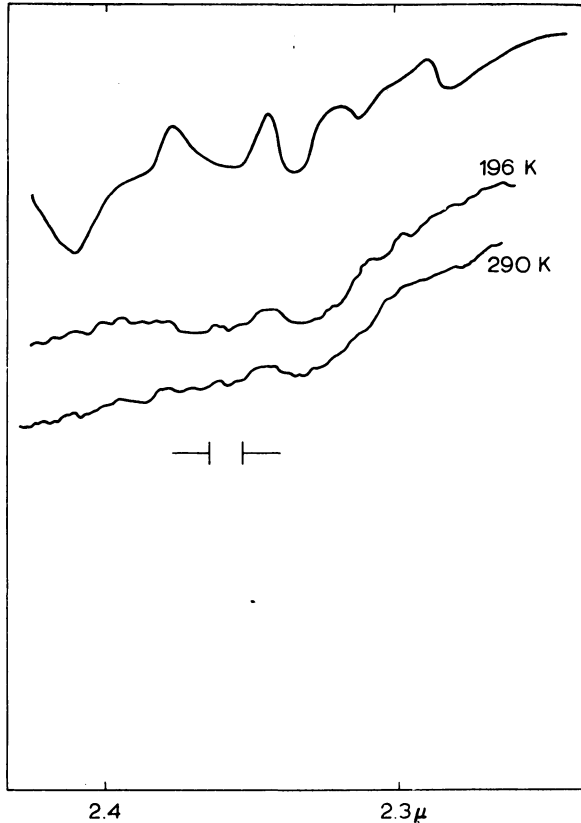


Fig. 13. Upper curve, the mean of 6 ratio spectra of Venus/Sun. The two lower curves are laboratory spectra of 79 cm atm of carbon monoxide. The spectral resolution is indicated on the figure. (From Sinton, 1963, *J. Quant. Spectrosc. Radiat. Transfer* 3, 551).

this region, it is difficult to make a positive identification of the substance; the proposed H_2SO_4 cloud particles are in qualitative agreement with Moroz's observations.

One of the most exciting observations reported in 1964 was made using a 30-cm aperture telescope carried by balloon to 26.5 km in the Earth's atmosphere. Bottema *et al.* (1964a) measured an absorption in the H_2O band at 1.13μ of $(10.5 \pm 0.5)\%$, "the same as that produced by $9.8 \times 10^{-3} \text{ gm cm}^{-2}$ of water vapor at atmospheric pressure." They estimated that there was "about $0.7 \times 10^{-3} \text{ gm cm}^{-2}$ of (telluric) water above the altitude of the balloon... The effective slant path through the atmo-

sphere of Vuens is calculated to be 3.82 times the vertical path." This means that if the telluric absorption is ignored, there is about 50μ of H_2O at 1 atm in a vertical column on Venus. Because the water absorption follows an approximately square root dependence on the pressure, Bottema *et al.* estimated that there would be 222μ of H_2O above clouds if they were at a pressure level of 90 mb or 52μ above clouds if they were at the 600 mb pressure level. "The respective mixing ratios would be 2.5×10^{-4} and 0.87×10^{-5} . A choice between these values, or in this range, must await more knowledge about the actual pressures."

Using the same balloon telescope technique, Bottema *et al.* (1964b) "obtained a reflection spectrum of the (Venus) clouds themselves ... The result was compared with reflection spectra of liquid water, ice, silica sand, liquid formaldehyde, oil, solid CO_2 ,

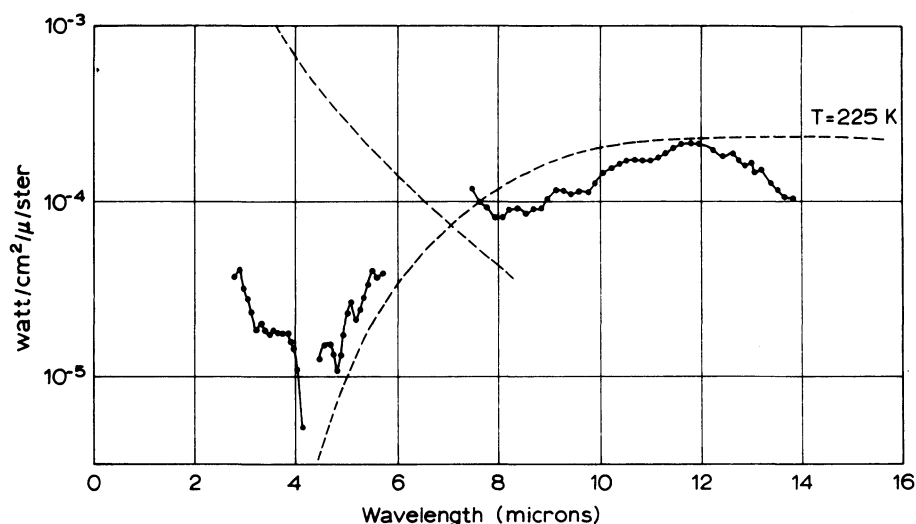


Fig. 14. Spectrum of Venus between 2.8 and 14 μ . The Planck curve for a blackbody at 225 K is shown and the calculated intensity of reflected sunlight for an albedo of 1 is indicated on the figure. (From Gillett *et al.*, 1968, *J. Atmosphere Sci.* **25**, 594.)

frozen CO_2 cloud, frost, and clouds of water droplets and ice crystals produced at various temperatures in our laboratory." They reported that they had "found agreement with the spectra of ice crystal clouds at temperatures (Sinton and Strong, 1960) comparable to those of the clouds on Venus." Indeed, the two spectra were in qualitative agreement, but it was far from a perfect match.

The amount of water vapor Bottema *et al.* had measured was in good agreement with Dollfus' measurement and their observations made by balloon presumably had the advantage of being taken above most of the telluric water vapor so that only minor corrections needed to be made for the telluric absorption. Öpik (1965) remarked, "The great value of the Strong-Bottema balloon results cannot be enough emphasized. They seem to have proven that water vapor, though in very small quantity, is present

above cloud level ...” On the other hand, Öpik disagreed with their identification of the cloud composition as being ice: “While water ice clouds have a high reflectivity in the blue-violet, Venus has a conspicuously low one; its spectral reflectivity curve in the optical region from violet to red, much better determined in absolute value than the relative figures found by Bottema-Strong in the infrared, disagrees completely with the reflectivity of water clouds, solid or liquid.” As we mentioned in the section on Cloud Composition, the debate on aqueous clouds on Venus is not over yet!

2.8. MORE SCATTERING IN THE ATMOSPHERE OF VENUS

Although Spinrad’s (1962a–e) measurements on the CO₂ band at 7820 Å had apparently shown that the scattering model (Chamberlain and Kuiper, 1956) yielded unrealistic temperatures for the atmosphere of Venus, Chamberlain (1965) attempted to reconcile the apparently conflicting infrared absorption data in terms of a scattering model. Chamberlain used essentially the same data as Kaplan (1961) had used with the reflecting layer model. “With the interpretation offered here, one must frankly admit that the CO₂ abundance and, to a lesser extent, the total gas pressure at the clouds are not nearly so well known as we have come to believe. But by way of compensation, the various conceptual difficulties that exist with the cloud reflection model are now readily disposed of.” This time Chamberlain suggested the use of a somewhat different solution to the equation of transfer (Chandrasekhar, 1950, p. 327) than had been used by Chamberlain and Kuiper (1956). Now it referred to the case where the Planck function increased linearly with optical depth, i.e.

$$B_\omega = B^0 + B^1 (1 - \varpi) t$$

which has a solution, for the emergent intensity, of the form

$$I(0, \mu) = (1 - \tilde{\omega})^{1/2} H(\mu) [B^0 + B^1 (1 - \tilde{\omega})\mu + B^1 (1 - \tilde{\omega})^{1/2} \alpha_1/2], \tag{12a}$$

where $\alpha_1 = \int_0^1 H(\mu) \mu \, d\mu$.

The intensity in the continuum is given by

$$I_c(0, \mu) = B^0 + B^1 \mu. \tag{12b}$$

While Chamberlain (1965) suggested that these relations could be used to find the temperature at the cloud tops, he did not use them himself.*

* However, one can use this formulation to derive a simple result which illustrates the effect of scattering on an absorption line profile: The residual intensity of the emergent flux in the line to the outward flux from the background continuum, i.e.

$$R \equiv \frac{F(0)}{F_c(0)} = \frac{\int_0^1 I(0, \mu) \mu \, d\mu}{\int_0^1 I_c(0, \mu) \mu \, d\mu}$$

From (12a) and (12b) we find

$$R = \frac{(1 - \tilde{\omega})^{1/2} [\alpha_1 (B^0 + B^1 \tilde{\omega} (1 - \tilde{\omega})^{1/2} \alpha_1/2 + \alpha_2 B^1 (1 - \tilde{\omega}))]}{B^0/2 + B^1/3}$$

Chamberlain (1965) used the expression found by Chamberlain and Kuiper (1956) for the line profile:

$$S(J) = 3^{1/2}(\mu + \mu_0)(1 - \varpi)^{1/2}$$

and, after some drastic assumptions about the behavior of collision-broadened lines, arrived at the conclusion that the equivalent width is given by

$$W(J) \simeq 10(\mu + \mu_0) \gamma(J) \langle 1 - \omega_J \rangle^{1/2}. \quad (13)$$

For the limiting case of pure absorption, $\tilde{\omega}_J \rightarrow 0$, this relation is clearly wrong. Since the equivalent width had been 'shown' to depend on the square root of the absorption coefficient, and hence on the square root of the line intensity, Chamberlain suggested that the following relation should hold:

$$W(\text{Venus}) = \text{const} [W(\text{lab})]^{1/2}. \quad (14a)$$

The laboratory equivalent widths were assumed to follow a linear absorption law. Chamberlain used Kuiper's (1962) laboratory measurements, which covered the spectral range 1.20–2.16 μ . These spectra had been obtained for a 80 m path of CO_2 at a pressure of 4 atm (or 0.32 km atm of CO_2). The pressure was high enough that all of the bands were unsaturated, with the exception of those near 2 μ , and their equivalent width was directly proportional to the amount of CO_2 . Chamberlain found that the relation

$$W(\text{Venus}) \simeq 4.5 [W(\text{lab})]^{1/2}, \quad (14b)$$

fits the unsaturated bands in Kuiper's laboratory spectra. While Chamberlain interpreted this result as a confirmation of his suggestion that scattering caused the Venus equivalent widths to follow a square root absorption law, it could also be interpreted as showing that the Venus spectra were saturated and followed a square-root absorption law because of a low pressure for line formation. The latter interpretation yields contradictory results, however: For a Venus air mass of 10, (14b) implies a vertical CO_2 abundance of 4 km atm formed at an effective pressure of 0.4 bar; some of the weaker bands in the Venus spectrum would be unsaturated under these conditions.

Chamberlain assumed that the level of line formation for the 8689 Å CO_2 band occurred at an optical depth of $\tau = 10$ and he estimated a total CO_2 abundance of

For an isothermal atmosphere, $B_1 = 0$,

$$R = 2(1 - \tilde{\omega})^{1/2} \alpha_1.$$

The first moment of the H function varies roughly as

$$\alpha_1 \sim 0.5(1 + \tilde{\omega}^2),$$

where this approximate relation is accurate within 15% for $0 < \tilde{\omega} < 1$. Hence the residual intensity can be crudely represented by

$$R(\tilde{\omega}) = (1 - \tilde{\omega})^{1/2} (1 + \tilde{\omega}^2).$$

As the scattering increases ($\tilde{\omega} \rightarrow 1$), the residual intensity decreases and the line becomes shallower.

5.6×10^3 cm atm. "If one took literally the assumption that the gas and particles are homogeneously mixed, then above the cloud tops ($\tau=1$) the abundance would be only 5.6×10^2 cm atm." This was considerably smaller than the abundance reported by Spinrad, but Chamberlain cautioned, "It is to be emphasized that no reliability whatever is to be placed on these numerical values. Several arbitrary assumptions and choices of parameters are involved in the calculation, and one could justifiably choose other parameters that would give widely different values. My point here is merely that, if the CO₂ bands are formed through multiple scatterings within the clouds, the CO₂ abundance becomes very uncertain and could easily be far smaller than the values generally quoted."

The high rotational temperature found by Chamberlain and Kuiper (1956) "suggests that the 8689 Å absorption band of CO₂ is normally formed at a mean temperature some 35 or 40K warmer than the cloud tops. This would, in a dry adiabatic temperature, occur at 4 or 5 km below the (cloud) tops at $\tau \sim 10$ in the near infrared. The fact that many scatterings are required for light to penetrate into and out of this depth means that the first scale height below the cloud top is *far* more effective in line formation than the atmosphere above the clouds."

Chamberlain also found that "Spinrad's measurements of line width, when interpreted by the theory of this paper, yield pressures of almost exactly one half the pressures (Spinrad) derived ... We at least can reaffirm Spinrad's conclusion that carbon dioxide is 'only a minor constituent of (Venus) atmosphere'."

The water vapor observations of Bottema *et al.* (1964a) presented a problem. Chamberlain decided that the relations he had used for weak CO₂ lines were not applicable to strong H₂O lines. "Hence, it may be legitimate to consider the H₂O lines as formed mainly by simple reflection above the cloud deck." The upper limit to the H₂O abundance fixed by Spinrad (1962a–e) and the high CO₂ rotational temperature reported by Chamberlain and Kuiper (1956) would be incompatible with the formation of H₂O lines at the same place in the atmosphere as the CO₂ lines. This implies that the water is not uniformly mixed in the atmosphere of Venus; it certainly isn't in the Earth's atmosphere. However, in the latter case, the same absorption laws apply to H₂O to CO₂. On Venus, things appeared to be different.

2.9. THE SEARCH FOR MINOR CONSTITUENTS CONTINUES

Spinrad and Richardson (1965) attempted to detect oxygen in the spectrum of Venus. They noted "that the pioneering attempt of St. John and Nicholson (1922) led to an extremely severe limit of 1 m atm O₂ on Venus." Once again the oxygen lines failed to appear. "The lack of displaced Cytherian O₂ lines near the tail of the telluric A band leads to a limit of 57 cm atm O₂, less than the terrestrial abundance by a factor of 2800. This result is in disagreement with the tentative detection of Venus oxygen by Prokofiev and Petrova (1962)." Spinrad and Richardson had estimated that a Venus O₂ line in the A band would be detectable if it had an equivalent width of 8 mÅ.

Moroz (1964a, b) continued his observations of the infrared spectrum of Venus in the wavelength ranges 1.2–2.5 μ and 2.8–3.8 μ . His measurements of the absorption by

CO₂ hot bands indicated a vibrational temperature $T_v = 250 \pm 20$ K. Moroz noted that this temperature was somewhat higher than the radiometric temperature (235 K) but lower than the mean rotational temperature (~ 300 K) reported by Spinrad. Moroz's result is in excellent agreement with the best current measurements of the rotational temperature (250 K).

Moroz noticed that the absorption of strong bands in the Venus spectrum appeared to be *linearly* related to their absorption in laboratory spectra. "This means that multiple scattering does not play an important part in the formation of these bands, or in other words, the absorption occurs above the cloud layer." Moroz estimated the CO₂ abundance in a vertical column to be $u = 25 \text{ gm cm}^{-2}$ at a pressure of $p = 0.3$ atm, assuming a carbon dioxide mixing ratio of 0.05 based on Spinrad's (1962a–e) results. ($1 \text{ gm cm}^{-2} = 51 \text{ m atm}$. For a carbon dioxide mixing ratio of 1.0, Moroz's data for Venus implied an abundance of 0.56 km atm at a pressure of 64 mb.)

Spinrad (1966) measured a 'hot' band of CO₂ (at 8736 Å) in the spectrum of Venus and reported a vibrational temperature of $T = 400$ K. He concluded that "The weak hot band lines originate deep in the Venus cloud layer, far below the 'cloud tops' at 230 K – the usually quoted infrared temperature." It is possible that some error was made in measuring the equivalent widths of the lines in this band, since later observations (Connes *et al.*, 1967) have indicated much colder temperatures (~ 250 K) for 'hot' bands.

Ground-based observers continued to search for water on Venus, encouraged by the apparently successful detection of it by the balloon-borne telescope. Belton and Hunten (1966) made photoelectric scans of the water lines at 8189.27 and 8193.00 Å. They noted that "the Venus lines are extremely weak and the spectra contain a considerable amount of noise." but were convinced that the elusive water lines on Venus were indeed visible in their spectra. "A preliminary estimate of the absorption in the red wing of the 8189 Å line on the May (1966) spectrum gives an equivalent width of 20 mÅ. The profile of the observed feature suggests an effective pressure of 5 atm." (The broad line profile could have been due to poor spectral resolution or to a blend with a solar line). Belton and Hunten reported, "we find that the estimated equivalent width corresponds to 317 μ of precipitable water in the total path. This result sets an extreme upper limit [sic] of 125 μ to the amount of precipitable water above the clouds."

Spinrad and Shawl (1966) confirmed the presence of water on Venus: "The equivalent width of the Venus λ8189 line is approximately 15 mÅ at the disk center ... The Venus component is rather broad and definitely seems stronger near the center of the planet's disk ... The center to limb change suspected for this Venus water line differs from the Venus CO₂ line situation; the λ8689 band CO₂ lines are quite uniform across the planet ..." Spinrad and Shawl reported 250 microns of precipitable water in the line of sight or 60 μ in a vertical path.

Owen (1967) pointed out that "both Belton and Hunten (1966) and Spinrad and Shawl (1966) used the water vapor line at 8189.272 Å as their principal evidence for the presence of water vapor on Venus." Owen's spectra of Venus showed "that a weak

absorption indeed appears at the correct position in the spectrum of Venus to correspond to a water vapor line formed in the atmosphere of that planet at an unshifted wavelength of 8180.272 \AA ... However, there is no line in the Venus spectrum that corresponds to the telluric (H_2O) feature at 8176.975 \AA , although the latter has an intensity virtually identical with that of $\lambda 8189.272$... In fact, no other Doppler shifted companions to the telluric water vapor lines are evident on this spectrum. It seems difficult to escape the conclusion that the feature appearing in the spectrum of Venus near 8189 \AA is simply a solar line that is normally hidden behind the much stronger telluric water vapor absorption (line)." Owen then proceeded to set an upper limit on the water vapor in the atmosphere of Venus, based on the absence of a Doppler shifted companion to the 8176.965 \AA line. He set 4 m\AA as an upper limit on the equivalent width, and obtained an upper limit of 64μ precipitable water in the total path, or 16μ in a vertical column. Hunten *et al.* (1967) replied that no Doppler shifted component of the 8189 \AA line was visible in the spectrum of Mercury and hence the feature they had found in the spectrum of Venus could not be a solar line.

2.10. THE DISCOVERY OF HCl AND HF

A surprising discovery about the composition of the atmosphere of Venus was made by W. S. Benedict. P. and J. Connes had obtained in 1966 the first really high resolution spectra of Venus at wavelengths longer than the photographic infrared. The individual rotational lines of the carbon dioxide bands were well resolved and many new CO_2 bands were discovered in the spectrum of Venus (Gray, 1966; Connes *et al.*, 1967). In addition to the readily identifiable CO_2 bands, there were some unidentified lines near 5750 cm^{-1} (1.74μ) which Benedict recognized as belonging to the HCl molecule. Further scrutiny of the spectrum revealed the presence of HF lines; neither HBr nor HI lines appeared. Connes *et al.* (1967) reported, "The HCl lines are consistent with 2 mm Amagat of that gas in the (total) optical path, at temperatures near 240 K and pressures near 0.1 atm, in a spectral region where the effective CO_2 path is 1.7×10^6 times as large. The less extensive HF data indicate about 0.02 mm Amagat of that gas." Connes *et al.* failed to detect any other hydrogen containing gases. "Among those which should have appeared on the spectra if present to more than a part per million are CH_4 , CH_3Cl , CH_3F , C_2H_2 and HCN." They did not detect any water vapor on Venus, but the spectra had been taken at a time when the terrestrial abundance of water vapor was large. There was 1 to 2 cm of precipitable (telluric) H_2O in the absorption path, which meant that the minimum amount of water which could be detected on Venus was 20μ . Hence Connes *et al.* (1967) reported an upper limit to the amount of water in the total path on Venus as 20μ . This upper limit was considerably smaller than the amount of water that Bottema *et al.* (1964a, b), Belton and Hunten (1966), and Spinrad and Shawl (1966) had reported detecting in the atmosphere of Venus. Connes *et al.* remark that "The evidence concerning H_2O on Venus is not strengthened by our results." They suggested that the low partial pressures of HCl and HF could be explained if these acids were "in weak solutions in clouds of ice water ..."

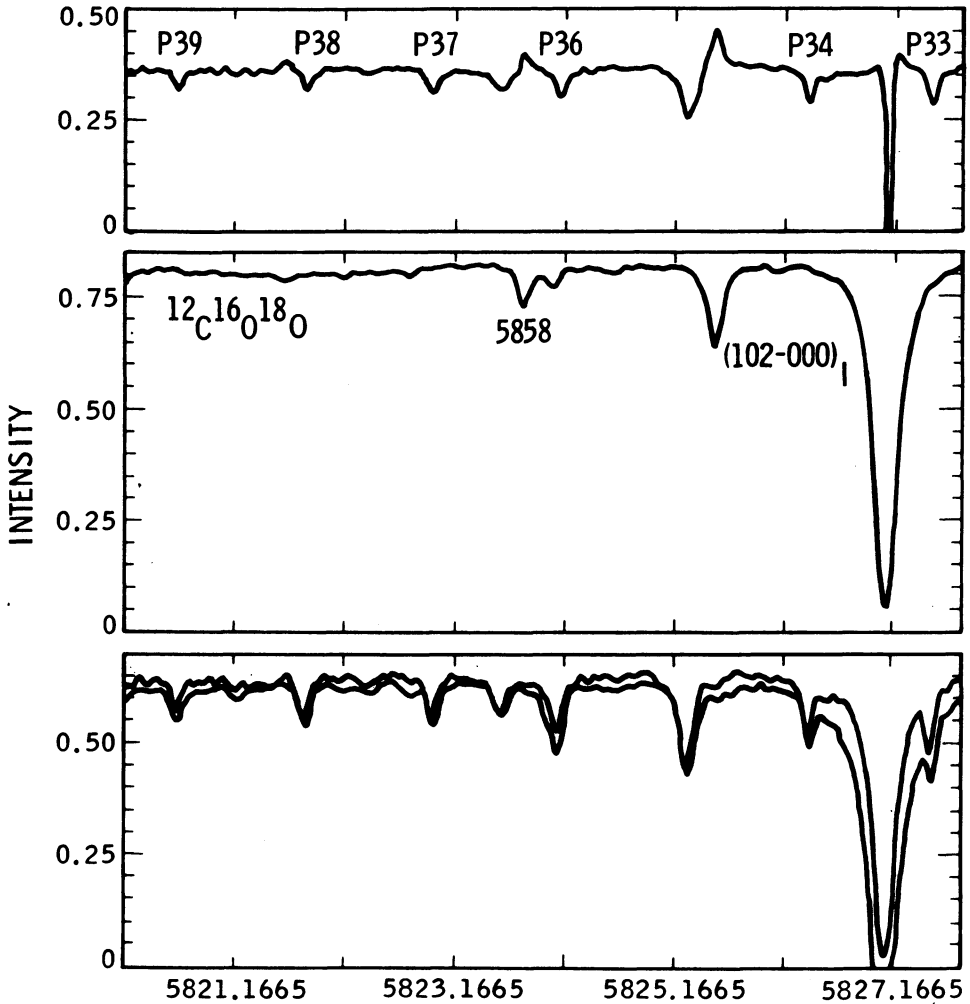


Fig. 15. A portion of the spectrum of Venus as measured by Connes *et al.* (1969). The upper part of the figure shows the ratio spectrum, Venus/Sun, of a few lines in the carbon dioxide band at 5858 cm^{-1} . The middle part of the figure shows the solar spectrum; the lower part shows two Venus spectra obtained for two different telluric air masses. (From Young, 1972, *Icarus* 17, 632.).

2.11. AIRCRAFT OBSERVATIONS OF VENUS

The next attempt to detect water on Venus was made by Kuiper and Forbes (1967). They measured the spectrum of Venus in the infrared from $1\text{--}2.5\ \mu$ with a spectral resolution of 20 cm^{-1} . The data were obtained during two flights of a NASA jet aircraft flying in the lower stratosphere. "The principal result is that in the observable part of the Venus atmosphere ($T \leq 320\text{ K}$) water vapor is essentially absent. It followed that the comparatively large amounts of water vapor derived spectroscopically from balloons and at ground-based observatories were spurious; and that atmospheric

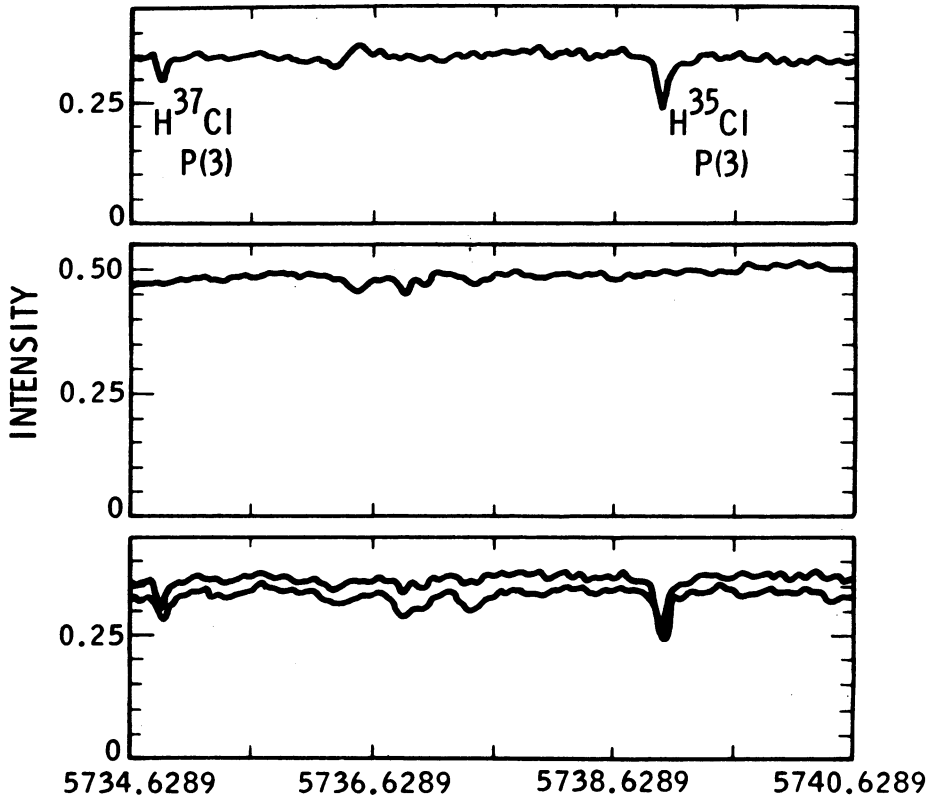


Fig. 16. A portion of the spectrum of Venus as measured by Connes *et al.* (1969). The upper part of the figure shows the ratio spectrum, Venus/Sun, of a few lines of hydrogen chloride. The middle part of the figure shows the solar spectrum; the lower part shows two spectra of Venus obtained for two different telluric air masses. (From Young, 1972, *Icarus* 17, 632.)

models of the planet, based on these earlier observations and invoking a large greenhouse effect by water vapor and water clouds, could not be valid." The result of Kuiper and Forbes "on the near absence of water vapor (amount $< 2 \mu$ in a 2-way transmission)" was in marked contrast with the comparatively large amounts reported by some ground-based observers, and was more in accord with the earlier observations when no detectable water could be found in the spectrum of Venus.

2.12. CARBON DIOXIDE, A MAJOR CONSTITUENT OF VENUS' ATMOSPHERE

One problem about the composition of the atmosphere of Venus was resolved by the spacecraft Venera 4: The atmosphere was found to be composed of $(90 \pm 10)\%$ CO_2 with less than 7% N_2 (Vinogradov *et al.*, 1968). Carbon dioxide was no longer a 'minor' constituent of the atmosphere. Once the mixing ratio became known, it was possible to obtain an upper limit for the pressure of CO_2 line formation simply from the mass of the gas corresponding to the observed absorption features. On this basis, Spinrad's (1962a-e) pressure estimates were a factor of 10-20 too large. Gray (1967)

estimated the pressure for line formation to be 40-65 mb and found that "the simple reflecting layer model would yield an amount of (CO₂) that is three times larger than the amount actually above this level." That is, the absorption path traversed by the reflected sunlight would be made three times longer (due to scattering) than the geometric path (without scattering). The influence of scattering did not change the CO₂ abundance in as drastic a way as Chamberlain (1965) had suggested it might.

2.13. WATER ON VENUS

On the other hand, the Venera 4 measurements posed a problem with regard to water. The space probe observations indicated more than 0.7 mg l⁻¹ of H₂O (at an altitude where the CO₂ density is 1.25 g l⁻¹) and less than 8 mg l⁻¹ of H₂O (where the CO₂ density is 3 g l⁻¹). This meant the H₂O volume mixing ratio could be as high as 1.4 × 10⁻³, or orders of magnitude larger than the spectroscopic observations had indicated. Water was detected by Venera 4 at the 700 mb level in the atmosphere of Venus. The carbon dioxide abundance above this level is 4 km atm_{sip}. If water were uniformly mixed in the atmosphere of Venus (which seems unlikely), there would be 560 cm atm_{sip}, or 4500 μ of precipitable water above the 700 mb level. (1 μ of precipitable water corresponds to 0.1245 cm atm_{sip} of water vapor.) Hence 450 μ of H₂O would be expected to be found above the 'cloudtop' at the 70 mb level. This large abundance could not have avoided being detected spectroscopically. The water on Venus appeared to be hiding below the clouds. Such behavior is not typical for aqueous clouds and is not easily explained.

Pollack and Wood (1968) compared the observed microwave brightness temperatures of Venus at a wavelength of 1.38 cm with theoretical calculations for a water line at that location. They found "an upper limit of 0.8% for the water vapor mixing ratio. This limit is consistent with the amount of water vapor detected by Venera 4, the existence of aqueous ice clouds, and a greenhouse effect caused by water vapor and carbon dioxide." More recent observations of Venus at 1.38 cm have been reported by Janssen *et al.* (1973). Their results showed "no evidence of water vapor in the lower atmosphere of Venus. The upper limit of 2 × 10⁻³ for the mixing ratio of water vapor is substantially less than the amounts derived from the Venera space probes (0.5 × 10⁻² and 2.5 × 10⁻²). This amount of water vapor cannot produce dense clouds, and it is doubtful that it may contribute significantly to a greenhouse effect."

Belton *et al.* (1968) obtained spectra of Venus for a few H₂O lines in the 8200 Å band and for two CO₂ bands near 1 μ. They chose to fit their observations with synthetic spectra computed for a semi-infinite, homogeneous, isotropically scattering atmosphere. Belton *et al.* noted that "our model is certainly oversimplified. Scattering in the Venus atmosphere is not isotropic, and the finite optical thickness of the cloud may well be an essential parameter (Sagan and Pollack, 1967). Homogeneity is also a doubtful assumption, which may have led to some disagreement with the observations. We regard our analysis (and the observations) as preliminary in nature, giving a point of departure for future work." Belton *et al.* reported "We have been able to deduce the following properties of the model which presumably describe the physical

state of the atmosphere at a level somewhere near to the visible cloud tops: A temperature of 270 K, an upper limit of 0.2 atm for the total pressure... the clouds on Venus are quite tenuous, the visibility in the cloud being of the order of 4 km. The model also implies that the CO₂ may be the major constituent in the atmosphere." They noted, "It is likely that the H₂O line (at 8189 Å) is formed at a level as low or even lower than the CO₂ lines... Neglecting the fact that the CO₂ and H₂O observations were made at widely separated times, we find (a mixing ratio) $N(\text{H}_2\text{O})/N(\text{CO}_2) = 10^{-4}$... If the H₂O absorption is actually at a lower level, the ratio will be an upper limit." This mixing ratio was much less than would be expected for water or ice clouds at 270 K; it is compatible with aqueous clouds at 213 K.

The model employed by Belton *et al.* indicated there were 0.4 km atm of CO₂ in a scattering mean free path $\lambda \geq 1$ km. The visual range is 4λ , so presumably their spectra would correspond to 1.6 km atm of CO₂ in an absorption cell.

Belton *et al.* suggested that one advantage of using synthetic spectra was that the continuum level is unambiguously defined. "Nowhere in the band does the intensity rise all the way to the continuum... It should be noted that this depression occurs in weak bands as well as the relatively strong ones observed here." In bands where the lines are poorly resolved, the instrumental profile can result in spectra that appear to have the 'continuum' depressed only if the 'continuum' is chosen to be at the point where the line absorption is minimum. If the continuum is picked as the level of zero line absorption on either side of the band, this problem is non-existent.

2.14. MEASUREMENT OF CARBON MONOXIDE AND TRACE CONSTITUENTS

Connes *et al.* (1968) reported, "The lines of the first overtone of CO are clearly resolved and appear prominently in high resolution interferometric spectra of Venus. Analysis of the lines of the principal isotopes shows that they are formed at cloud level, with an effective temperature of 240 K, and a total effective CO path of 13 cm Amagat. Comparison with CO₂ lines yields a CO/CO₂ ratio of 45 parts per million." They remarked that "As with the HCl/CO₂ ratio obtained previously (Connes *et al.*, 1967), this value is independent of the details of the radiation transfer process in the Venus clouds, as long as the CO and CO₂ are uniformly mixed." Connes *et al.* had obtained an effective pressure of 60 mb but noted that "the effective pressure defined by our analysis procedure is *not* synonymous with a mean pressure of line formation. It is, in fact, a lower limit."

Belton (1968) questioned the results of Connes *et al.* (1967, 1968) since they "have interpreted their observations of HCl and HF with the Ladenburg and Reiche curve of growth which applies to the reflecting layer model." In deriving the mixing ratios reported for the minor constituents, Connes *et al.* had, in fact, compared lines of CO₂ with lines of the minor constituents having the same equivalent width: "It is possible, however, to establish several matches between lines in the 002 band of ¹²C¹⁶O¹⁸O at 4640 cm⁻¹ and the CO band, which are of nearly equal strength for Venus. The most favorable one is the RO line at 4640.21 cm⁻¹ whose $W = 0.096$ cm⁻¹ is 4 percent less than the corresponding line in CO... We obtain $N_{\text{CO}}/N_{\text{CO}_2} = 4.4 \times 10^{-5}$. Other com-

parisons give similar ratios." Belton (1968) thought "it very difficult to obtain precise measurements of the equivalent widths of the individual lines. In fact, some investigators (Belton *et al.*, 1968) have considered the measurement of the equivalent widths in the CO₂ bands to be so imprecise that they abandoned the usual method of interpreting absorption lines, i.e., the curve of growth..." Belton then proceeded to "develop a theory of the curve of growth from pressure broadened lines of arbitrary strength in a semi-infinite, homogeneous, non-conservative, isotropically scattering atmosphere." This approximate theory resulted in a curve of growth remarkably similar to the Ladenburg-Reiche (no scattering) curve, except the curve predicted smaller equivalent widths for the scattering case when the total path length L is replaced by $\eta_0(\kappa + \sigma)^{-1}$. Here η_0 is an effective air mass and $(\kappa + \sigma)^{-1}$ is a mean free path. Belton (1968) had required his theoretical formulation of the curve of growth to approach the Ladenburg-Reiche curve for the case of no scattering, as it should, so the resemblance between the curves was not surprising. He then proceeded to re-analyze the data of Connes *et al.* For HCl, Belton found "the pressures derived here for the scattering model are all *larger* by a factor of 2 or 3, than the effective pressures found by Connes *et al.* ... one expects to derive pressures which are about 2 times *lower* than would be the case for the reflecting layer model."

It should be noted that Belton's 'curve-of-growth' technique required that the particle single scattering albedo be known before the pressure for line formation could be determined. He assumed that the continuum albedo was in the range 0.90 to 0.9999; the pressures ranged from 0.14 atm to 1.2 atm. Belton remarked, "As the continuum albedo at 1.7 μ (where the HCl absorbs) has not been measured, it is difficult to chose which of the pressures... is correct for Venus." However Belton was able to obtain "essentially the same" mixing ratios for the minor constituents as those reported by Connes *et al.* (1967, 1968) by suitable choices of the continuum albedo. Belton (1968) decided that "the applications of the curves of growth developed here leads to a surprisingly consistent picture of the physical conditions in the clouds of Venus. The exception is that this model, while giving the correct sense to the variation of line absorption with phase, does not agree quantitatively with the available observations." It should be recalled that it was the variation of equivalent widths of the lines with phase, which led Chamberlain and Kuiper (1956) to reject the idea that the cloud tops acted as a reflecting layer and to suggest that the observations could be explained if an appropriate scattering model was used. Thus the idealized model used by Belton (1968) obviously required some modification in order to get quantitative agreement with the observations.

2.15. ROTATIONAL TEMPERATURE OF CO₂ BANDS

The next observations of Venus were made by Gray and Schorn (1968) of the three CO₂ bands near 1 μ . These measurements indicated the rotational temperature was $200\text{K} < T < 250\text{K}$, or significantly lower than the temperatures reported by Chamberlain and Kuiper (1956) or by Belton *et al.* (1968). On the other hand, the temperatures reported by Gray and Schorn were in fairly good agreement with temperatures mea-

sured further out in the infrared (Sinton, 1962a, b; Moroz, 1964b; Connes *et al.*, 1967, 1969). These first temperatures obtained by Gray and Schorn assumed that the equivalent widths of the lines followed a square-root absorption law and might be referred to as temperatures for a 'radiative transfer' model.

Gray (1969) then described a general curve of growth technique for finding rotational temperatures which is essentially model independent. The basic idea is to compare two lines in the same CO₂ band, which have identical line strengths, half-widths

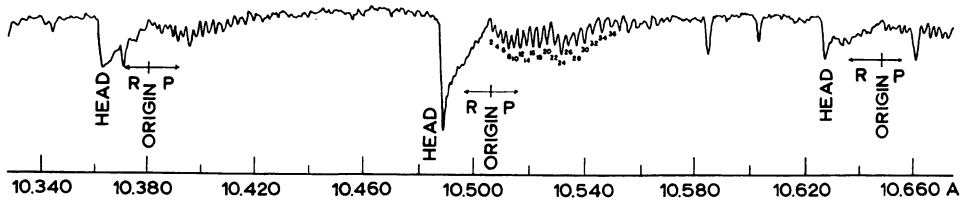


Fig. 17. Spectrum of Venus showing the three carbon dioxide bands near 1 μ . (From Kuiper, 1962, *Comm. Lunar Planet. Lab.*, No. 15.)

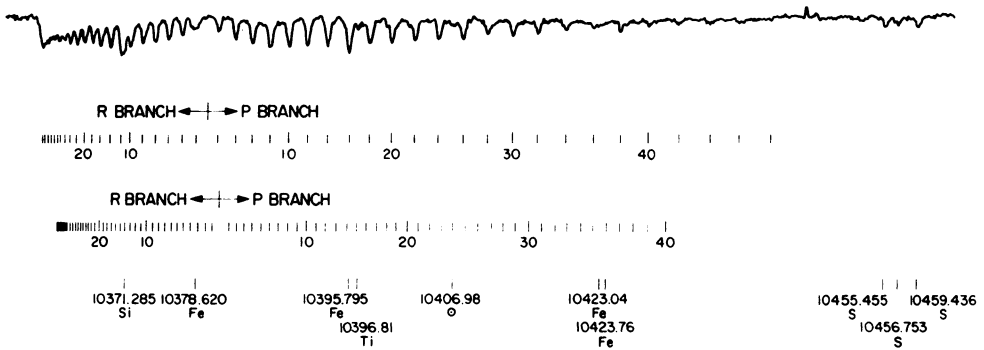


Fig. 18. Spectrum of Venus showing the carbon dioxide band at 10362 \AA , at somewhat higher resolution than is shown in Figure 17. (From Schorn *et al.*, 1970, *Icarus* 12, 391.)

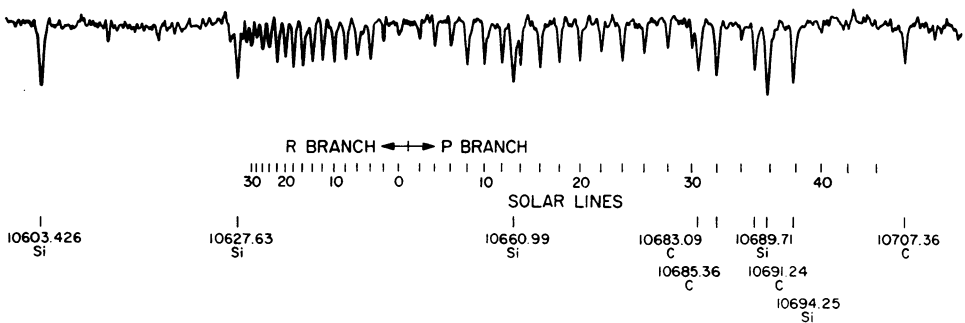


Fig. 19. Spectrum of Venus showing the carbon dioxide band at 10627 \AA , at somewhat higher resolution than is shown in Figure 17. (From Schorn *et al.*, 1971, *Icarus* 14, 21.)

and equivalent widths. The two lines will have come from different lower state rotational energy levels, $E_{\text{rot}}(J)$, with the line intensity given by

$$S(J) = \frac{S(v) F(J)}{Q_{\text{rot}}(T)} \exp - \left(\frac{E_{\text{rot}}(J)}{kT} \right). \quad (15)$$

Here $S(v)$ is the strength of the band

$$S(v) = \sum_J S(J), \quad (16)$$

and $F(J)$ is related to the f -number of the rotational transition. For the 1μ CO_2 bands:

$$F(J) = J \text{ for the } P \text{ branch,} \quad (17a)$$

and

$$F(J) = J + 1 \text{ for the } R \text{ branch.} \quad (17b)$$

The rotational energy levels are given by

$$E_{\text{rot}}(J) = hcBJ(J + 1). \quad (18)$$

Thus when two lines within the same band have the same value of $S(J)$, $S(J_1) = S(J_2)$, the rotational temperature is given by

$$T = \beta [J_1(J_1 + 1) - J_2(J_2 + 1)] [\ln \{F(J_1)/F(J_2)\}]^{-1}, \quad (19)$$

where $\beta = hcB/k = 0.5614 \text{ K}$ for ground state CO_2 bands.

If both of the lines have the same halfwidth, and are formed at the same pressure level in the atmosphere, then they will have identical equivalent widths. In practice, the variation of the line halfwidth $\gamma(J)$ with the rotational quantum number J is easily taken into account (Young, 1970a). Gray (1969) assumed that the equivalent width could be related to the line intensity by

$$W \sim S^b,$$

where b is the local value of the slope of the curve of growth. The major assumption involved in this procedure is that of local thermodynamic equilibrium, and subsequent measurements (Connes *et al.*) have given no indications to the contrary.

In order to obtain a better value for the rotational temperature than might be found by only comparing two lines in a band, Gray (1969) showed how a least-squares fit could be made to the equivalent widths of all of the lines in the band. This was an iterative procedure, involving both T and b , but it was rapidly convergent. Gray applied the curve of growth analysis to the measurements made by Spinrad (1962a-e) of the ten old Mt. Wilson plates for the 7820 \AA band of CO_2 . The results indicated that most of the old data followed a nearly square root absorption law and the temperatures were generally lower than those reported by Spinrad. The average temperature found by Gray was $T_{\text{rot}} = 293 \pm 20 \text{ K}$ while Spinrad found $T_{\text{rot}} = 338 \pm 23 \text{ K}$. Here the quoted errors refer to one external standard deviation since the old data indicated a pro-

nounced variation in the temperature with time. Subsequent observations (Young, 1972) have not shown any significant variation in the temperature and the average temperature (based on 197 measurements) is 250 ± 2 K.

2.16. THE CURVE OF GROWTH

It is surprising how long it took for a well-known astrophysical technique (van der Held, 1931; Menzel, 1936; Unsöld and Struve, 1949) to 'trickle down' from stellar spectroscopy to the interpretation of planetary spectra. The curve of growth represents the increase in the equivalent width of a line as a function of the number of absorbing molecules, for a fixed line intensity, with the line half-width as a parameter. For a gravitational atmosphere, the effect of scattering is as follows: As a few scatterers are introduced into the atmosphere, the apparent absorption path is increased and the equivalent widths of the lines are increased. The curve appears to be shifted vertically from its position with no scattering. When sufficient scattering particles are added, that optical depth unity is reached at a level in the atmosphere where the pressure is less than the surface pressure, the apparent absorption path will reach a point where it is shorter than in the non-scattering case, and the curve of growth will be shifted below the curve for no scattering. Adding more scatterers to the atmosphere, or increasing the scattering optical depth, will shift the curve of growth even further below the curve for no scattering. In a real atmosphere, there are two reasons for the decrease in equivalent width with the increase of τ_s (for $\tau_s > 2$): One is the decrease in the amount of gas traversed by the reflected light. The second is the decrease in the effective pressure for line formation; this causes the lines to be more saturated and hence makes their equivalent widths smaller. The scattering optical depth has to be known before the amount of gas can be uniquely determined. To date, the scattering model atmospheres which have been used to interpret Venus spectra have used various assumed values for the albedo. This involves assuming both the scattering optical depth and some fixed mixing ratio for the number of scattering particles relative to the number of absorbing molecules. The results obtained from these models clearly depend on how realistic these assumptions are.

2.17. MORE OBSERVATIONS OF VENUS

Cruikshank and Kuiper (1967) looked for SO_2 near 3000 \AA , but none could be detected in the atmosphere of Venus. They concluded "that the upper limit of the abundance of this gas in the complete transmission path through the upper Venus atmosphere is 0.05 mm atm ," and estimated that the mixing ratio was less than 5×10^{-8} . Cruikshank (1967) also looked for the sulphur compounds COS and H_2S in the spectrum of Venus without success. He estimated that there was less than 0.5 cm atm of COS and less than 1 m atm of H_2S in the total absorption path, and the upper limit to their mixing ratios was 10^{-8} and 2×10^{-4} , respectively.

Owen (1968a, b) searched for carbon suboxide, water vapor, the absorption features reported by Kozыrev, and the night sky emission spectra of Venus. He failed to detect any of the spectral features he had hoped to detect.

Hanel *et al.* (1968) measured the emission spectrum of Venus between 8–13 μ with an interferometer. They observed “the broad absorption-like feature centered at 890 cm^{-1} (11.2 μ)... This observation confirms the existence of this phenomenon. The feature may be caused by a residual ray effect in the material composing the clouds.” Hanel *et al.* measured a brightness temperature of “about 250 K.” Gillett *et al.* (1968) had obtained spectra of Venus from 2.8–14 μ , with a resolution of $\lambda/\Delta\lambda = 50$, and reported a brightness temperature of about 225 K for the 8–13 μ region. Presumably the difference in the brightness temperatures reported by various observers is due to their calibration procedures, rather than to Venus herself.

Belton and Hunten (1968) searched for oxygen on Venus. They scanned a 9 Å region in the A band and no features due to O₂ on Venus could be seen. They estimated “that lines of 3 mÅ equivalent width should be readily detected...” Belton and Hunten (1968) found an upper limit of 12.5 cm atm in the total absorption path or less than 3 cm atm_{stp} in a vertical column. Comparison of the upper limit found for O₂ by Belton and Hunten (from $W \leq 3$ mÅ) with that found by Spinrad and Richardson (from $W \leq 8$ mÅ) reveals that the line intensity used by the former is too large by a factor of 2 (Margolis *et al.*, 1971). The upper limit obtained by Belton and Hunten should be revised upward; there is less than 24 cm atm_{stp} in the total absorption path. Belton and Hunten (1968) found an O₂/CO₂ mixing ratio based on the amount of CO₂ reported by Connes *et al.* (1967) of 3.3 km atm in the total path. They applied an air-mass correction to O₂ but not to CO₂ and reported an O₂/CO₂ mixing ratio of ‘less than 2×10^{-5} ’ (Belton and Hunten, 1969). This upper limit on the mixing ratio must be increased to 7×10^{-5} , if the CO₂ abundance were the same on the dates of the two observations; however, this assumption has no justification. Belton and Hunten (1969) reported a mixing ratio of “less than 8×10^{-5} for the scattering model,” the two methods of data reduction gave essentially the same result. Interestingly enough, this upper limit on the mixing ratio is *identical* to that reported by Spinrad and Richardson (1965) which had been obtained from the ratio of the O₂ partial pressure (upper limit) to the “total pressure at the base of the line formation,” and the latter had been over-estimated.

Schorn *et al.* (1969a) carried out an extensive series of spectroscopic observations of Venus during 1967, in a search for water vapor. From April to June, their results were negative, giving an upper limit of < 32 μ in April and May and < 16 μ in June, for the amount of precipitable H₂O in a vertical path. In November and December, they detected water on Venus, 30–40 μ . “Our conclusion is that the observable amount of water vapor ‘above the clouds’ of Venus varies significantly... Comparison of H₂O variations with variations in CO₂ bands, UV cloud activity and, possibly, millimeter wavelength observations should be most informative... The questions of why and how these variations occur should have a definite bearing on the composition of Venus’ clouds and the structure of its atmosphere... Extensive and homogeneous series of observations are required to make progress in this area, as with most problems in planetary astronomy... ‘One shot’ observations, no matter how well conceived and executed will not be of much help.” Since the question of whether the clouds are

aqueous or not had been settled to everyone's satisfaction, more 'one shot' observations would be published.

Schorn *et al.* (1969b) noted, "Compared to the theoretical work done on the subject, relatively few observations have been made of the 7820 Å carbon dioxide band in the spectrum of Venus." They observed this band during 1967 and found no significant variation in the rotational temperature with the phase angle i of Venus for $50^\circ < i < 90^\circ$. Schorn *et al.* reported an average rotational temperature of $T_{rot} = 242 \pm 2$ K (formal standard deviation) from 18 observations. They commented that

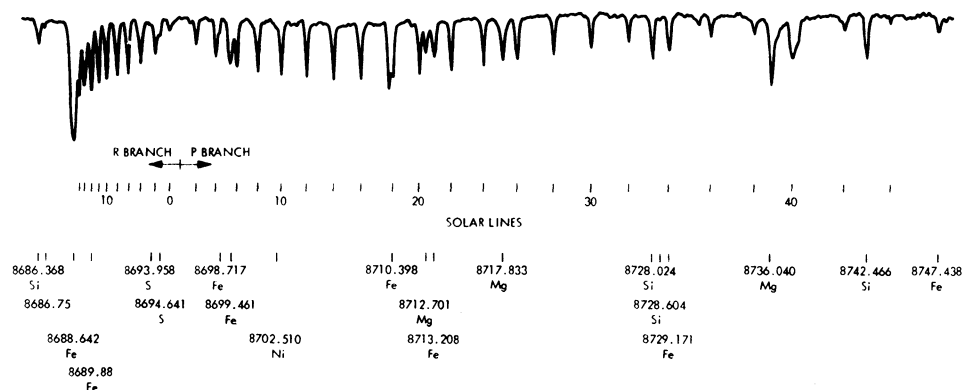


Fig. 20. Spectrum of Venus showing the carbon dioxide band at 8689 Å. (From Young *et al.*, 1969, *Icarus* 11, 390.)

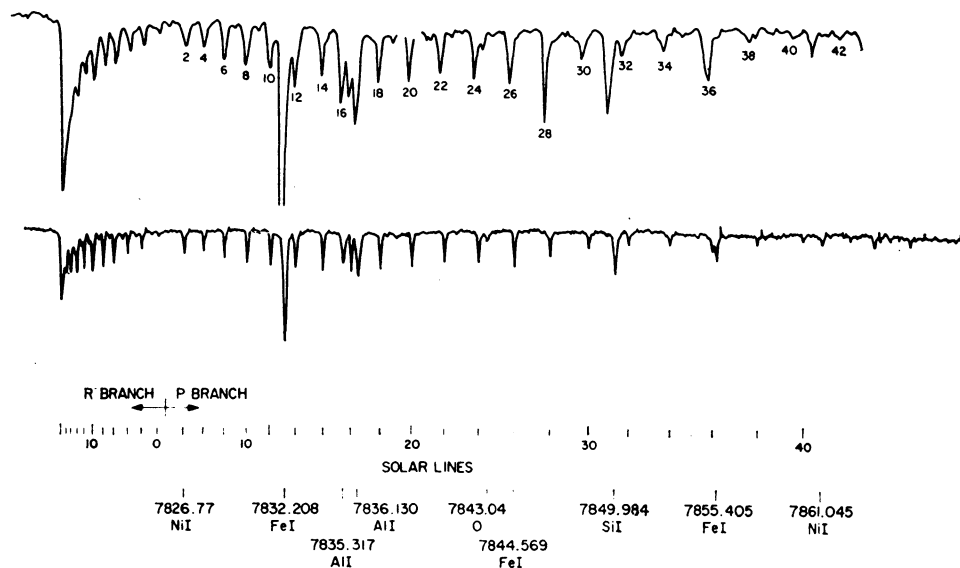


Fig. 21. Spectra of Venus showing the carbon dioxide band at 7820 Å. The upper spectrum was taken by Dunham and the lower spectrum is at somewhat higher resolution. (From Schorn *et al.*, 1969b, *Icarus* 10, 241.)

“the amount (of CO₂) appeared to vary significantly with time.” At a particular phase angle, the abundance varied by almost a factor of two.

Gray *et al.* (1969) measured rotational temperatures for the CO₂ band at 7883 Å in the spectrum of Venus. From 12 observations, they found an average “rotational temperature of 244 ± 10 K (standard deviation and no significant temporal variation of temperature . . . the amount of carbon dioxide in the absorption path appears to vary with time.”

Young *et al.* (1969) found an average rotational temperature for Venus of “ $T_{\text{rot}} = 238 \pm 1$ K (standard deviation) based on 23 plates of the 8689 Å CO₂ band . . . The variation of the equivalent width of the 8689 Å band with Venus phase is seen to agree generally with the observations of Kuiper; the equivalent width decreases with increasing phase angles. . . . As Kuiper (1952) noted in discussing his measurements, there is considerable fluctuation in the equivalent width at a particular phase angle.”

Kuiper *et al.* (1969) reported that spectra of Venus, which had been taken during flight of the NASA jet aircraft, definitely showed the presence of water vapor on Venus. There was 5μ of precipitable H₂O in the total absorption path. “Since the corresponding figure for CO₂ is about 4 km atm,” the mixing ratio is 1.5×10^{-6} . “The observed amounts of trace constituents, such as H₂O, will, for constant mixing ratios, vary with the amount of CO₂ observed, known to be variable from day to day as well as systematically with phase.” Thus, even if H₂O were uniformly mixed in the atmosphere of Venus, the observed amount of water would appear to vary. Kuiper *et al.* (1969) also identified “numerous vibrational bands of CO₂,” and bands belonging to CO, HCl, and HF in their spectra of Venus.

Young (1969) used the Venus spectra of Connes *et al.* (1969) to determine the rotational temperature of an isotopic CO₂ band at 2.21μ . The result, $T = 245 \pm 3$ K, was in good agreement with the temperature of $T = 240$ K reported by Connes *et al.* (1967, 1968). Schorn *et al.* (1970) reported a rotational temperature of $T = 237 \pm 12$ K for Venus from 15 spectra of the CO₂ band at 1.0362μ . Belton *et al.* (1968) had observed this band but did not attempt to find a temperature for Venus since “The entire spectrum was not of such high quality as the 1.05μ band.” Young *et al.* (1970a) also studied the CO₂ band at 1.0488μ in the spectrum of Venus. From 31 plates, they found an average rotational temperature of $T = 237 \pm 3$ K, which was considerably lower than the temperature of $T = 270 \pm 25$ K, which Belton *et al.* (1968) had found by matching one spectrum of Venus. The temperatures measured by Young *et al.* gave no indication of varying with time. Young *et al.* (1970b) found the CO₂ bands at 1.2030μ and 1.2177μ gave similar temperatures: $T = 236 \pm 5$ K based on 10 spectra. Young (1970a) again used the Venus spectra of Connes *et al.* (1969) to find the rotational temperature of a CO₂ band at 1.71μ . This band indicated a temperature of $T = 242 \pm 2$ K in agreement with the results found from 0.72μ to 2.21μ . All the previous estimates for rotational temperatures, by *all* investigators, had assumed the variation of the line widths with rotational quantum number could be neglected. Young (1970b) found that including this effect, the CO₂ band at 1.71μ indicated a tempera-

ture of $T = 249 \pm 3$ K. "The results indicate that the effect (of variation in the line widths) on the temperature is slight, increasing it by 3%."

Schorn *et al.* (1971) reported that 17 spectra of Venus for the 1.0627μ band of CO_2 indicated a rotational temperature of 241 ± 3 K (or 250 ± 3 K when the correction for variable line widths is applied). The temperature did not show any variation for Venus phase angles $26^\circ \leq i \leq 164^\circ$, while the CO_2 abundance "appeared to vary significantly with the phase of Venus and also with the time of observation."

Young *et al.* (1971) reported on observations of Venus during 1968 and 1969. Twenty-two spectra of the CO_2 bands at 7820 \AA and 7883 \AA gave an average rotational temperature of 251 ± 2 K and 257 ± 4 K, respectively. These temperatures were found using a variable rotational line half width. They noted that the equivalent widths of these CO_2 bands varied significantly, "but there was little correlation between that variation and the phase angle of Venus" for $10^\circ < i < 126^\circ$. Young *et al.* noted that "theoretical calculations (Chamberlain, 1970) based on observations of the 8689 \AA band, predict a much greater variation with phase than we observe. Because of the great care with which we measured the equivalent widths and evaluated the systematic errors involved, we find the difference between theory and observations to be remarkable."

Beer *et al.* (1971) measured the continuum absorption by Venus in the $3\text{--}4 \mu$ region. Their spectra had a resolution of $\lambda/\Delta\lambda = 5000$ and "in order to improve the signal-to-noise ratio, an average was made of the three spectra (obtained on one day) together with one obtained a few days earlier." "The resulting spectrum of Venus ($2400\text{--}3100 \text{ cm}^{-1}$) showed strong absorption in the region $2400\text{--}2600 \text{ cm}^{-1}$, minimum absorption between 2880 cm^{-1} and 2980 cm^{-1} and the suggestion of a weak absorption feature at 3050 cm^{-1} . Beer *et al.* (1971) suggested that these features might be due to bicarbonates. They found "that NaHCO_3 and KHCO_3 show some of the requisite (spectral) characteristics but that the frequency match is inadequate."

Lewis (1972) commented, "Recently Beer *et al.* (1971) have published a high resolution spectrum of Venus in the $3.1\text{--}4.2 \mu$ region, which clearly shows a strong cloud absorption band centered at 3.9μ and a possible weak band centered at $\lambda < 3.2 \mu$. They match the Venus reflection spectrum to laboratory transmission spectra of NaHCO_3 and KHCO_3 , which have strong, broad absorption bands centered at 4.03 and 3.83μ , respectively, and weak absorption bands at 3.45 and 3.40μ , respectively. It is striking that the *highest* reflectivity found in the Venus spectrum is from 3.35 to 3.48μ , corresponding precisely to the locations of known *absorption* bands in the alkali bicarbonates." Hence, the suggestion of bicarbonate clouds was ruled out. Lewis went on to note that the spectrum of HCl dissolved in dioxane ($\text{C}_4\text{H}_{10}\text{O}_2$) gave a satisfactory fit to the spectrum of Venus obtained by Beer *et al.*

Young and Young (1973) cautioned, "In any serious attempt to determine spectroscopically the composition of the Venus clouds, the entire spectrum of Venus should be matched, not just a single feature ... To illustrate precisely how weak the spectroscopic evidence is, we have chosen to 'fit' the Venus spectrum at 11.2μ ." Young and Young showed that the Venus absorption band at 11.2μ could be fit by six substances,

several of which had an absorption at 3.9μ . Of the substances they considered, sulphuric acid had a spectrum which most closely resembled the spectrum of Venus.

Regas *et al.* (1972) observed portions of the 1.0488μ CO_2 band over several nights. "The region P22-P32 was scanned on October 20, 21, 22 and the region P34-P42 on October 23 and 24," 1967. The "spectra were combined and smoothed ..." To interpret their observations, Regas *et al.* computed synthetic spectra. They used the spacecraft results for their model atmosphere: "A tropopause temperature of 238 K, a tropopause pressure of 0.258 atm, a surface temperature of 770 K, a surface pressure of 97 atm, and a composition by volume of 95% CO_2 and 5% N_2 . In addition, in our models, we had an isothermal region above the tropopause and an adiabatic region below the tropopause with a lapse rate of 8.83 K km^{-1} ." For their scattering model calculations, Regas *et al.* (1972) remarked, "Our clouds have tops and bottoms. ... the cloud top is that point in the atmosphere above which there is a negligibly small optical depth, say $\tau < 0.01$." For a dust cloud model with the cloud bottom at the surface of the planet, Regas *et al.* found there was an entire set of pairs of scattering coefficients and cloud top pressures that gave a satisfactory fit to their observations. Similar results were obtained for a condensation cloud model. They reported, "We found that the cloud top pressure was significantly lower than the tropopause pressure for all of our acceptable models." The maximum cloud top pressure, according to Regas *et al.* was 0.157 atm, "... a quantity independent of the scattering model ..." They chose "the model of the Venus clouds that would have the weakest possible water line (at 8189 \AA) and yet still give a good match to our CO_2 observations. Using a cloud layer model with a cloud top pressure of 0.37 atm, a cloud top temperature of 238 K, and no water vapor above the clouds, we found the 0.8189μ H_2O line has an equivalent width of 100 m\AA , about 7 times larger than (the largest value reported for) the observed line. ... it is unlikely the clouds are pure water ice."

The fact that many observers have reported day-to-day variations in the equivalent width of CO_2 bands in the spectrum of Venus strongly suggests that observations from several days should not be averaged as Regas *et al.* have done. Results obtained from averaged spectra can give us some idea about the conditions at the cloud tops, but it is not clear that this really represents average conditions.

Moroz (1971) reported variations in the CO_2 abundance over different areas of Venus, based on his spectroscopic observations of the 1.58 and 1.61μ CO_2 bands. Based on 4 days' observations, Moroz concluded "the Venusian cloud layer is lower over the polar than over the equatorial region of the planet ... the pressure at the top of the clouds is nearly 3 times larger in polar regions than in equatorial regions ... the difference in height of the top of the cloud level between high and low latitudes is $\Delta z \simeq 7 \text{ km}$." Hunt and Schorn (1971) argued that "the variations over the disk of the planet of the equivalent widths must be associated with the dynamical properties of the Venus atmosphere ... but its precise meaning in terms of the variation of the structure of Venusian cloud layers remains unresolved at present." The observations of the CO_2 band at 8689 \AA made by Young *et al.* (1969) do not support the suggestion that the cloud layer is consistently lower over the polar regions than over the equatorial region.

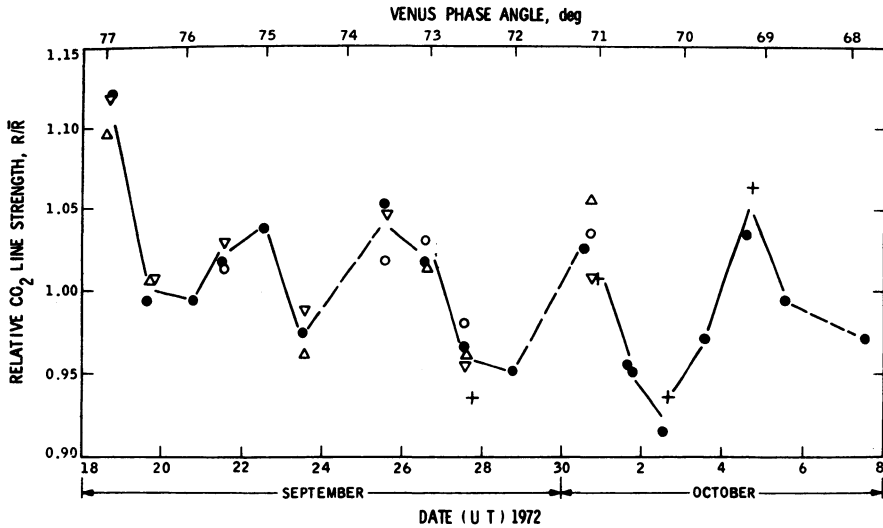


Fig. 22. Measurements of the day-to-day variation in the strength of the carbon dioxide band a 8689 Å, relative to the strength of the neighboring solar lines in the spectrum of Venus. The different symbols refer to different locations on Venus: equator (open circles), northern latitude (triangle, point up) southern latitude (triangle, point down), standard meridian (solid circles and crosses, the latter taken at slightly higher resolution). (From Young *et al.*, 1973, *Astrophys. J.* **181**, L5.).

Fink *et al.* (1972) analyzed infrared spectra of Venus produced by a Fourier spectrometer flown aboard the NASA jet aircraft. They obtained "an improved determination of water vapor for the Venus atmosphere of $1.6 \pm 0.4 \mu$ of precipitable water in the total path." The CO_2 abundance in the total path was 3.6 km atm which "leads to a volume mixing ratio of 0.6×10^{-6} for water vapor, assuming the two (gases) to be uniformly mixed." Using a homogeneous, isotropic, semi-infinite scattering model with $\tilde{\omega}_c = 0.999$ gave "a mixing ratio of 1.0×10^{-6} , in close accord with the above number." Fink *et al.* remarked, "It is quite obvious that our result is one-to-two orders of magnitude below any other determination except that of Kuiper whose amount was obtained with the same airborne instrument as the present result. We have no physical explanation for this discrepancy except the comment that every 'determination' of the water vapor in the Venus atmosphere appears to have been the experimental limit of detectivity for the particular method. Our results, of course, refer to an average over the illuminated portion of the disk..." Fink *et al.* suggested that "an extremely hygroscopic material" is needed as a cloud constituent if their results are to be reconciled with "a high total water content (as measured by the Russian Venera atmospheric entry probes)." They made calculations for $\text{H}_2\text{O-HCl}$ droplets and found their water vapor abundance "will not allow a lower cloud deck to be composed of $\text{H}_2\text{O-HCl}$ droplets." Fink *et al.* remarked, "Although HCl failed in lowering the vapor pressure sufficiently, one can think of more powerful 'drying agents' such as sulfuric acid for example. A rough calculation showed that an 80% by weight solution of sulfuric acid can dry the upper atmosphere sufficiently to give agreement with our

measured abundance and yet keep the total amount in the lower atmosphere high enough to yield the Venera spacecraft water measurements. Such an idea must, however, most certainly be rejected, due to other chemical complications this model would introduce." They concluded, "Since neither a cold trap nor a hygroscopic material is presently plausible in the Venus atmosphere, our mixing ratio for water of about 1 ppm must extend through the whole Venus atmosphere... Venus is severely depleted in water."

Owen and Sagan (1972) reported upper limits for the abundances of many minor constituents in the atmosphere of Venus based on ultraviolet spectra obtained from the orbiting astronomical observatory. They noted that, "In all cases, we have adopted a simple reflecting layer formalism. We feel that greater sophistication is unjustified and unnecessary at present (Regas and Sagan, 1970a, b; Sagan and Regas, 1970)." These are included in Table III along with upper limits which have been set for various substances which have not been detected in infrared spectra of Venus.

Young *et al.* (1973) reported that observations of the CO₂ band at 8689 Å showed "the apparent strength of CO₂ absorptions in the spectrum of Venus varies by 20%, in a period of 4 days. The variations are synchronous over the disk, and thus represent a fundamental dynamical mode of the atmosphere... To produce the observed changes

TABLE III
Composition of the atmosphere of Venus

Molecules observed in the atmosphere of Venus above the clouds

Gas	Mixing ratio	Total amount (cm atm _{stp})	Pressure (mb)	Temperature (K)	Reference
CO	$4.5 \pm 1.0 \times 10^{-5}$	13	60	240	Connes <i>et al.</i> (1968)
	$5.1 \pm 0.1 \times 10^{-5}$	20	36	249 ± 3	Young (1972)
CO ₂	0.97 ± 0.04	Vinogradov <i>et al.</i> (1970a, b)
	...	$3.3 \pm 0.3 \times 10^5$	100	240 ± 10	Connes <i>et al.</i> (1967)
	...	$2.8 \pm 0.4 \times 10^5$	60	240	Connes <i>et al.</i> (1968)
	...	$4.1 \pm 0.1 \times 10^5$	36	249 ± 3	Young (1972)
	...	$0.9 - 5.5 \times 10^5$	100	245	Fink <i>et al.</i> (1972)
HCl	6×10^{-7}	$1.9 \pm 0.4 \times 10^{-1}$	80	270 ± 30	Connes <i>et al.</i> (1967)
	$4.2 \pm 0.7 \times 10^{-7}$	$1.7 \pm 0.3 \times 10^{-1}$	160	240 ± 16	Young (1972)
HF	5×10^{-9}	$2.5 \pm 0.5 \times 10^{-3}$	100	240	Connes <i>et al.</i> (1967)
	7×10^{-9}	$2.9 \pm 0.2 \times 10^{-3}$	67	249 ± 3	Young (1972)
H ₂ O	1.1×10^{-2}	...	600	295	Vinogradov <i>et al.</i> (1968)
	10 ⁻⁶	...	10000	500	Vinogradov <i>et al.</i> (1970a, b)
	10 ⁻⁴	35	Dollfus (1963a, b)
	2.5×10^{-4}	100	90
	8.7×10^{-6}	25	600	...	Bottema <i>et al.</i> (1964a, b)
	10 ⁻⁴	39	Belton and Hunten (1966)
	10 ⁻⁴	30	Spinrad and Shawl (1966)
2×10^{-6}	0.6	Kuiper (1969)	
H ₂ O	2×10^{-5}	5	Schorr <i>et al.</i> (1969a, b)
	0.6×10^{-6}	0.2	100	240	Fink <i>et al.</i> (1972)

Table III (Continued)

Molecules not observed in the atmosphere of Venus above the clouds

Gas	Maximum Mixing ratio	Maximum amount (cm atm _{stp})	Reference
CH ₂ O	10 ⁻⁶	10 ⁻¹	Owen and Sagan (1972)
CH ₃ and aldehydes	10 ⁻⁶	10 ⁻¹	Owen and Sagan (1972)
CH ₄	10 ⁻⁶	3 × 10 ⁻¹	Connes <i>et al.</i> (1967)
CH ₃ Cl	10 ⁻⁶	3 × 10 ⁻¹	Connes <i>et al.</i> (1967)
CH ₃ F	10 ⁻⁶	3 × 10 ⁻¹	Connes <i>et al.</i> (1967)
CH ₃ COCH ₃ and ketones	10 ⁻⁶	10 ⁻¹	Owen and Sagan (1972)
C ₂ H ₂	10 ⁻⁶	3 × 10 ⁻¹	Connes <i>et al.</i> (1967)
C ₂ H ₄	10 ⁻⁵	2	Kuiper (1952)
C ₂ H ₆	10 ⁻⁵	4	Kuiper (1952)
C ₃ O ₂	10 ⁻⁷	10 ⁻²	Owen and Sagan (1972)
HCl	10 ⁻⁶	10 ⁻¹	Owen and Sagan (1972)
HCN	10 ⁻⁶	3 × 10 ⁻¹	Connes <i>et al.</i> (1967)
H ₂ O	6 × 10 ⁻⁶	2	Connes <i>et al.</i> (1967)
H ₂ S	2 × 10 ⁻⁵	8	Owen (1967)
H ₂ S	10 ⁻⁷	10 ⁻²	Owen and Sagan (1972)
N ₂	2 × 10 ⁻²	...	Vinogradov <i>et al.</i> (1970a, b)
NH ₃	3 × 10 ⁻⁸	10 ⁻²	Kuiper (1962)
NO	10 ⁻⁶	10 ⁻¹	Owen and Sagan (1972)
NO ₂	10 ⁻⁸	10 ⁻³	Owen and Sagan (1972)
N ₂ O	6 × 10 ⁻⁴	200	Kuiper (1952)
N ₂ O ₄	4 × 10 ⁻⁸	4 × 10 ⁻³	Owen and Sagan (1972)
O ₂	7 × 10 ⁻⁵	24	Belton and Huntten (1968)
O ₃	3 × 10 ⁻⁹	3 × 10 ⁻⁴	Owen and Sagan (1972)
SO ₂	5 × 10 ⁻⁸	5 × 10 ⁻³	Cruikshank and Kuiper (1967)
	10 ⁻⁸	10 ⁻³	Owen and Sagan (1972)

in line strength, the cloud tops must be moving up and down by 0.2 scale height, or over 1 kilometer, all over the disk at once." Their observations were made when the phase angle of Venus was $68^\circ < i < 72^\circ$.

2.18. INTERPRETATION OF SPECTRA OF VENUS

Sagan and Pollack (1969) used an empirical fit to laboratory measurements of CO₂ bands to interpret published spectra obtained by Kuiper (1962). They found effective pressures for line formation to be between 48 and 110 mb based on Kuiper's spectra for the CO₂ bands near 1.2 μ and 1.6 μ . Sagan and Pollack (1969) suggested that "a multiple scattering model is not the only one capable of explaining the phase dependence of the absorption line strength. Either a single cloud layer with individual clouds having a large range of altitudes or a model with two cloud layers might account for the phase observations."

Young (1970c) used the data of Schorn *et al.* (1969a, b, 1970) and Young *et al.* (1969, 1970a, b) to study the change in the effective pressure for line formation in the atmo-

sphere of Venus as a function i , the Venus phase angle. "The data are analyzed by two techniques: a reflecting layer model for lines with a Voigt line profile and a scattering model for lines with a Lorentz line profile." The effective pressure for line formation for a strong line ($P\ 16$) in the $1.0488\ \mu\text{ CO}_2$ band decreased from 95 mb near superior conjunction ($i=26^\circ$) to 19 mb near inferior conjunction ($i=164^\circ$) according to the reflecting layer model. Use of Belton's (1968) scattering model indicated a decrease from 173 mb ($i=26^\circ$) to 89 mb ($i=164^\circ$). The trend is the same for the two models, except the scattering model predicts that the lines are formed at higher pressures than is predicted by the reflecting layer model.

Chamberlain (1970) developed "an approximate analytic theory for the formation of spectral absorption lines in a hazy atmosphere with isotropic scattering and a homogeneous mixture of scattering and absorbing matter." He once again used (9a) and van de Hulst's approximation (8) for the H functions. Chamberlain chose to parameterize the absorption lines by two quantities analogous to the parameter x used for pure absorption:

$$q_c \equiv \frac{Su}{\pi\gamma\tau_c}$$

and

$$q_t \equiv \frac{Su}{\pi\gamma(\tau_s + \tau_c)},$$

where τ_s is the scattering optical depth and τ_c is the continuum absorption optical depth (in Chamberlain's notation, $q = q_c$ and $w = q_t$).

Chamberlain (1970) found that the equivalent of a weak line, for $q_c \ll 1$ and $q_t \ll 1$, varied as

$$W = \frac{Su}{(\tau_s + \tau_c)} [1 + f_1(\tau_s, \tau_c, \mu, \mu_0)], \quad (20)$$

where the function $f_1(\tau_s, \tau_c, \mu, \mu_0)$ depends on μ, μ_0 for $\tau_s = 0$. For $\tau_s \gg \tau_c$, so $q_c \gg 1$ and $q_t \ll 1$, Chamberlain found the equivalent width varied as

$$W = \frac{Su}{(\tau_s + \tau_c)} [1 + f_2(\mu, \mu_0)] + \left[\frac{Su\gamma}{\pi(\tau_s + \tau_c)} \right]^{1/2} f_3(\tau_s, \tau_c, \mu, \mu_0). \quad (21)$$

For strong lines, with $q_c \gg q_t \gg 1$, Chamberlain found the equivalent width varied as

$$W = \left[\frac{Su\gamma}{\pi(\tau_s + \tau_c)} \right]^{1/2} f_4(\tau_s, \tau_c, \mu, \mu_0). \quad (22)$$

The functions f_1, f_2, f_3 and f_4 can be found in the paper by Chamberlain (1970) and will not be given here. Chamberlain and Smith (1970) applied "this 'two-parameter theory' to the CO_2 absorptions on Venus to see whether a consistent picture can be

derived from all the available data without introducing additional, *ad hoc* assumptions.” Chamberlain and Smith reanalyzed the spectrum obtained by Belton *et al.* (1968) for the 1.05 μ CO₂ band. Chamberlain and Smith remarked that the analysis of this spectrum by Belton *et al.* was not unique. They found “for $1 - \tilde{\omega} \ll 1$ that lines that have

$$\left[\frac{Su\gamma}{\pi(\tau_s + \tau_c)} \right]^{1/2} \ln \left(\frac{\tau_c}{\tau_s + \tau_c} \right) = \text{const.}$$

possess nearly identical equivalent widths.”

Chamberlain and Smith (1970) concluded that it is “not possible to distinguish among any of the models (which ranged from $\tilde{\omega}_c = 0.95, p = 0.422$ atm up to $\tilde{\omega}_c = 0.995, p = 0.050$ atm) with the 1.05 μ profile alone.” They obtained a qualitative fit to the observed phase variations of the CO₂ band at 8689 Å (Chamberlain and Kuiper, 1956) for $\tilde{\omega}_c = 0.997$, and remarked, “It is clear that the phase variation has little dependence on line strength in this band and that a rather good fit with the data is possible.”

In order to fit the phase dependence of the equivalent width in the 1.6 μ bands measured by Moroz (1967), Chamberlain and Smith found that the continuum albedo must be very close to unity. For $\tilde{\omega}_c = 1.000$, the equivalent-width varies as $(\mu + \mu_0)$, in qualitative agreement with Moroz’s observations. There is considerable scatter in the measured equivalent widths, but the phase variation computed for $\tilde{\omega}_c = 1.000$ is in much better agreement with Moroz’s observations than the phase variation computed for $\tilde{\omega}_c = 0.999$. In order to confirm this large value for the continuum albedo at 1.6 μ , Chamberlain and Smith computed synthetic spectra to match the CO₂ band at 1.71 μ observed by Connes *et al.* (1969). They remarked, “It appears again that we must have $\tilde{\omega}_c \gtrsim 0.999$ to obtain a satisfactory fit for the 1.71 μ band.” Belton (1968) had found the same band required $\tilde{\omega}_c = 0.991$, but Chamberlain and Smith (1970) showed that this value of $\tilde{\omega}_c$ predicted less absorption for the strong lines of the band than was observed. Chamberlain and Smith concluded, “For a pure-scattering model atmosphere, the gaseous abundance ‘above the cloud tops’ is a concept without meaning, since the clouds have no well defined tops... The equivalent abundance of CO₂ cannot be ascertained to an accuracy better than a factor of 2.” They also concluded that their scattering model could fit all the data, “provided the scattering albedo is close to unity around 1.7 μ .”

Tables of the Bond albedo for isotropically scattering semi-infinite atmospheres are given by Young (1970b) and Chamberlain and Smith (1970); the latter tables are the most extensive.

Chamberlain and Smith (1972) investigated “the hypothesis that the CO₂ absorption lines in Venus’s spectrum could be formed between an upper thin cloud and a lower thick one.” They found, “The phase effect depends on the amount of incident radiation that is able to penetrate the upper cloud and then emerge in the direction of the observer. It depends not only on the geometry itself but also on the optical thickness of the upper cloud, which acts as a diffusing screen... In view of the day-to-day

scatter in W (the equivalent width of a CO_2 band), it would be difficult observationally to distinguish between the two (phase) curves” for a homogeneous model and a two-cloud model. They concluded “that a satisfactory two-cloud model for the Venus atmosphere may be derived from existing data. However, this model is not unique, but is highly dependent on built-in assumptions regarding this type of model. Thus, the two-cloud model fits the observational data about as well as a single cloud model. More sophisticated and accurate spectroscopic data would undoubtedly narrow the acceptable ranges of parameters, but the question of uniqueness will be difficult to establish for any specific case.”

Hunt (1972a) suggested that “models based upon homogeneous isotropically scattering atmospheres cannot be used to reproduce observed spectroscopic features of phase effect and the shape of spectral lines for weak *and* strong bands;” an inhomogeneous (gravitational) model of a planetary atmosphere is required. Hunt used a model where the cloud did not extend either to the surface of the planet or to the top of the atmosphere. Based on this model, he arrived at the following conclusions: “For fixed continuum properties, the phase effect increases with increasing line strength. Increasing the mean free path of the cloud particles (which is equivalent to decreasing the particle concentration) increases the phase effect ... The introduction of continuum absorption reduces the phase effect ...”

Hunt (1972b) reported, “We have shown that only observations of the phase variations of the CO_2 bands in the Venus spectrum can provide the information for a unique identification of the structure of the cloud layers. It is proved that Venus cannot have a single dense cloud layer, but must have two scattering layers: a thin aerosol layer situated in the lower stratosphere, overlying a dense cloud deck.” Hunt noted that “The effect of an optically thin aerosol on the level of line formation is most noticeable for large phase angles, $i > 110^\circ$, say. The absorption lines are then formed higher in the atmosphere than they would be if only one cloud were present.” However, for small phase angles, if the phase curve shows “a positive gradient then this is evidence of a distinct aerosol layer ... If there is a negligible gradient, then the aerosol is continuous down to the main cloud top.”

Regas *et al.* (1973) showed that the same kind of phase variation “may be due to the strong backward lobe in the Venus cloud phase function and that the two cloud layers are not necessarily required.” Hunt (1973) disagreed.

3. Summary

One may well ask, what is the value of infrared spectroscopy for studying a cloud-covered planet like Venus? Progress in learning about the physical and chemical nature of her atmosphere has not been rapid, using this approach. And, as is true any time complicated phenomena are studied, the infrared spectra have sometimes completely led people astray.

The most sought-after substance in the atmosphere of Venus, H_2O , is either undetectable, variable, or present in such amounts that the clouds of Venus can/

cannot be aqueous. All of these views have been put forth on the basis of Venus spectra. Similarly, spectra of Venus have been used to support various other hypotheses about the cloud composition.

Spectroscopy is a useful tool in the search for minor atmospheric constituents. Besides the controversial observations of water vapor, few minor constituents have been found on Venus: CO, HCl and HF. The major atmospheric constituent, CO₂, discovered spectroscopically in 1932, was shown 'to be a minor constituent' in the 1960's. Only the Venera spacecraft measurements served to dispell that erroneous notion. Various theoretical models have been proposed to intepret the observations but there has been no agreement on the 'right' one. Both the reflecting layer model (Kaplan, 1961; Sagan and Pollack, 1969) and a scattering model (Chamberlain and Smith, 1970) have been shown to 'fit all the observational data' provided certain assumptions are made about the nature of the clouds. Fortunately, both approaches give approximately the same results for the abundance of minor constituents relative to carbon dioxide.

The reasons for the slow progress in understanding Venus are threefold: observational, theoretical, and psychological. On the observational side, it has turned out that spectroscopic data which have an excellent signal-to-noise ratio but low spectral resolution cannot be used to distinguish uniquely between different theoretical models of the Venus atmosphere. Extremely high resolution spectra are required. Unfortunately, some observers have led the theoreticians astray by overestimating the quality of their data. On the other hand, some theoreticians have dismissed perfectly good observations under the assumption that the data were 'noisy' because conditions on Venus appeared to vary on a short time scale, a situation that could not occur in their models. There has been a profusion of crude, oversimplified models which have 'explained' discrepancies between theory and observation as due to effects not included in the theory. Thus there has been a tendency to claim 'agreement' with the observations prematurely. Finally, not only have wrong interpretations of the data been widely accepted at various times, but some correct interpretations have been rejected for long periods of time. What interpretation is 'acceptable' has been colored by prejudices (Venus is/isn't like the Earth, the curve of growth does/doesn't apply to a scattering atmosphere, etc.) so that major questions appear to have been decided more on emotional than on rational grounds.

In the future, it would help if observers would strive to put realistic error estimates on their data; if theoreticians would state clearly the kind and accuracy of observations needed to test their models; and if everyone would adopt a more critical attitude instead of jumping to conclusions.

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Appendix A: The Air-Mass Function

(*A. T. Young*)

The air-mass for a plane-parallel atmosphere, neglecting refraction, is well known to be proportional to the secant of the zenith angle. But real planetary atmospheres are curved, not flat; and the rays of light are also curved by atmospheric refraction.

Usually, the atmospheric curvature exceeds the ray curvature, especially if we restrict our attention to situations where the atmospheric density (and hence the refraction) is small. Even at sea level on Earth, the curvature of a horizontal ray is only one-sixth that of the atmosphere (Newcomb, 1906), so that neglect of refraction is not a serious error. For the atmosphere of Mars, and the visible part of Venus' atmosphere, the refraction is much less, and the atmospheric curvature somewhat greater; thus the straight-ray approximation is even better for these planets.

Even if we neglect refraction, we must specify the law of density variation with height, for the ray passes more obliquely through the lower than through the upper layers of the atmosphere. If the density variation is $\rho(h) = \rho(0) \cdot x(h)$, the air mass is

$$F(z) = \frac{1}{H} \int_0^{\infty} x(h) ds, \quad (\text{A1})$$

where the height of the homogeneous atmosphere is

$$H = \int_0^{\infty} x(h) dh, \quad (\text{A2})$$

and the element of path length along the ray, ds , is related to h , z , and the planetary radius R by the law of cosines:

$$(R + h)^2 = R^2 + s^2 + 2Rs \cos z. \quad (\text{A3})$$

We note that $x(h)$ is the density, normalized to unity at $h=0$; and

$$ds = \frac{(R + h) dh}{(R^2 \cos^2 z + 2Rh + h^2)^{1/2}}. \quad (\text{A4})$$

Lambert (1760) expanded ds in a power series to obtain

$$F(z) = A \sec z - \frac{1}{2} B \sec z \tan^2 z + \dots, \quad (\text{A5})$$

where the coefficients A, B, \dots are integrals of functions containing the unknown density law $x(b)$, but not z . Lambert proposed to obtain these coefficients from observations of atmospheric extinction. On the other hand, Bouguer (1760) assumed an exponential atmosphere, i.e.,

$$x(b) = \exp(-h/h_0), \quad (\text{A6})$$

for which $H=h_0$ of course. From this assumed law, Bouguer obtained explicit values of Lambert's coefficients by performing the necessary integrations. However, as Bemporad (1901) pointed out, Bouguer made an unfortunate change of variable in performing the integrations, and thus obtained incorrect results (in error by a factor of 2 even in the second term); the correct series is

$$F(z) = \sec z - \frac{h_0}{R} \sec z \tan^2 z + 3 \left(\frac{h_0}{R} \right)^2 \sec^3 z \tan^2 z - \dots \quad (\text{A7})$$

In the meanwhile, however, Laplace (1805) had shown the connection between the air-mass problem and the atmospheric-refraction problem, and all subsequent air-mass calculations included the effects of ray curvature. These numerous investigations, which are reviewed by Schoenberg (1929), culminated in the work of Bemporad (1904), which has been enshrined in all subsequent handbooks up to the present as *the* air-mass function.

Bemporad's mean air-mass tables have been so widely reprinted that their limitations are often overlooked. They are based on a mean atmospheric model that is not strictly correct, although the consequent error in $F(z)$ is less than half a percent, according to Abbot *et al.* (1922). Because the refraction depends strongly on pressure and the effective height of the atmosphere depends strongly on temperature, Bemporad gives corrections that depend on these quantities; unfortunately, they are usually ignored. The calculations assume the absorbing species are uniformly mixed, which is seriously in error for ozone, water vapor, and aerosols; the corrections can be comparable to the difference between the mean $F(z)$ and $\sec z$ (Abbot *et al.*, 1922; Young, 1973). Finally, one must remember that the argument of Bemporad's tables is the apparent (refracted) zenith angle, not the true value.

As Bemporad (1904) points out, expansions like Equation (A7) are unsuitable near the horizon, because each term becomes infinite at $z=90^\circ$. Bemporad uses various auxiliary variables to achieve convergence. However, for grazing incidence it is convenient to develop the air-mass problem somewhat differently, as has been done by Fabry (1929) for a ray that passes completely through an exponential atmosphere, reaching at its lowest point a pressure p :

$$F(p) = \sqrt{2\pi R/h_0} p/p_1, \quad (\text{A8})$$

where p_1 is a reference level above which the zenithal air-mass is taken as unity.* For an observer at the level p , the horizontal air-mass is just half the value of Equation (A8). As Fabry was concerned only with the upper atmospheres of planets, he neglected ray curvature. More general formulae, including refraction, are given by Link (1969).

* Fabry actually obtains h_0 times (A8) for the equivalent path length at pressure p_1 .

The classical problem of the exponential atmosphere without refraction was belatedly solved once again by Chapman (1931), whose air-mass function is

$$f(R/h_0, z) = F(z) \tag{A9}$$

in our notation. Chapman deduces Fabry's (1929) formula for the horizontal air-mass, Bemporad's (1901) corrected version of Bouguer's (1760) formula, and various other series expansions that are somewhat less convenient for numerical evaluation (as they are expressed in terms of higher transcendental functions) than the conventional formulae.

It has unfortunately become the custom to attach Chapman's name to air-mass functions in the English aeronomical literature; the Bouguer-Bemporad function is called 'the ordinary Chapman function', and the air-mass for a nonexponential (but still nonrefracting) atmosphere is called 'a generalized Chapman function' by Green and Martin (1966). They treat an atmosphere whose density profile is a sum of exponential distributions with different scale heights, as well as some other analytical density distributions.

However, as Link (1969) points out, there are many practical problems which require the use of actual, not analytical, densities. The exponential model has long been criticized for neglecting not only the variation of temperature with height, but also that of the local gravitational acceleration. The physical crudeness of such models is sometimes concealed by the deceptive accuracy of published tables, which often extend to 3 or 4 decimal places.

The exponential, nonrefracting atmosphere is again treated by Fesenkov (1955), who expresses the Bouguer-Bemporad series in terms of $\sec z$ alone. As Fesenkov's interest is in the twilight sky brightness, he also gives the air-masses above various heights [i.e., the integral in Equation (A1) for nonzero lower limits]. The twilight problem for Venus, looking in from space instead of up from the planet, is treated in detail by Schilling and Moore (1967) and by Link (1969, pp 216–225).

Finally, a most practical method of evaluating the Bouguer air-mass is to neglect h in the numerator and h^2 in the denominator of Equation (A4), which allows the integration to be done in closed form, giving

$$F(z) = (\sec z) [\pi^{1/2} X \exp(X^2) \operatorname{erfc}(X)], \tag{A10}$$

where

$$X = (R/2 h_0)^{1/2} \cos z, \tag{A11}$$

and

$$\begin{aligned} \operatorname{erfc}(X) &= 1 - \operatorname{erf}(X) \\ &= 2\pi^{-1/2} \int_X^\infty \exp(-t^2) dt. \end{aligned} \tag{A12}$$

This approximation is derived at length by Green and Martin (1966), who call this approximation 'the essential part of the Chapman function,' and more simply by

Young (1969), who gives the necessary series expansions for large and small X . The series expansion of the correction factor in brackets in Equation (A10) for large X gives the principal terms in Fesenkov's (1955) series, but with an error of order (h_0/R) in each coefficient; it is equivalent to replacing $\tan^2 z$ by $\sec^2 z$ in the accurate Bouguer-Bemporad series (A7). Green and Martin (1966) compare the approximate and exact values, for three values of R/h_0 (which they call x ; they also use a parameter β such that $\beta^2 = 2X^2$): the relative error is, at most, of order h_0/R , as would be expected from the above discussion. For $z < 90^\circ$, the approximate values of F are too small. However, Equation (A10) gives Fabry's value (A8) for twice the horizontal air-mass. Furthermore, the effect of refraction can be approximately included by adopting a larger effective value of R , whose reciprocal is the *difference* in curvatures of the planet and a horizontal ray (Young, 1973).

To illustrate the effects of atmospheric curvature, we consider observations of Venus at large phase angles, i . The *minimum* curvature correction occurs halfway between limb and terminator, where $z_c = i/2$. Above the clouds we have $R \approx 6100$ km, $h_0 \approx 5$ km, so Equation (A8) gives about 88 for twice the horizontal air-mass. (This is the air-mass at the cusp, at all phases.) The curvature correction is one percent at $\sec z_c = 3.5$ or $z_c = 73^\circ.3$, $i = 146^\circ.6$; the average correction over the disk will be somewhat larger, of course. The correction exceeds ten percent at $\sec z_c = 11$, $i = 170^\circ.6$. The maximum phase angle at which Venus has been observed spectroscopically is near 175° ; here $F(z_c) \approx 17$ but $\sec z_c = 23$, a difference of about one third. Thus, contrary to Huntén's (1971) suggestion that $\sec z$ is an adequate approximation, the curvature effects are appreciable.

Finally, let us consider the depth to which a tangential ray can penetrate the atmosphere of Venus. According to Link (1969, p. 214) the maximum refraction observed in transits of Venus is about a minute of arc, which corresponds to a maximum pressure of about 5 millibars of CO_2 . This is an order of magnitude *lower* than the cloud-top pressure deduced spectroscopically. Equation (A8) then tells us that we are seeing the Sun through some 8.8 times as much gas as lies above the cloud tops, which is not much more than we see at moderate phase angles; we cannot expect to find minor constituents by looking tangentially through Venus' atmosphere.

Presumably the tangential ray is being cut off by aerosols above the main cloud deck. Schilling and Moore (1967) find from twilight phenomena that appreciable aerosol extends at least 15 km (3 scale heights) above the clouds. If the aerosol were distributed with the same scale height as the gas, we would have $e^{-3} \approx 1/20$ as much at this height as at the cloud tops. This agrees reasonable well with the pressure deduced from the refraction, about 1/10 of the cloud-top value. Since we are seeing nearly a hundred times as much of this material at grazing incidence, the normal-incidence optical depth of the aerosol would be about 0.01 – that is, the 'high scattering layer' observed at inferior conjunction is practically invisible under ordinary circumstances.

From the above examples, it can be seen that observations near inferior conjunction can, by the relation (A1) between $\rho(h)$ and $F(z)$, provide information on the vertical structure of Venus' atmosphere.

Appendix B: Preliminary Spectroscopic Data for Carbon Dioxide Bands Observed in High Resolution Spectra of Venus

(*P. Connes, J. Connes, W. S. Benedict, and L. D. Gray*)

The spectrum of Venus was used to find spectroscopic constants for comparatively weak bands of CO₂. These bands are difficult to measure in the laboratory, whereas the atmosphere of Venus provides an absorption path more than a km long at an effective pressure on the order of a tenth of an atmosphere. We have tabulated preliminary values of spectroscopic data obtained from the spectrum of Venus measured by Connes *et al.* (1969). Additional data for spectral regions not measured by Connes *et al.* can be found in the tabulations of McClatchey *et al.* (1973), Courtoy (1959), and Young *et al.* (1970c).

The data we have tabulated allow one to compute the intensity and position of any carbon dioxide line which appears in the spectrum of Venus, for the spectral regions covered by the atlas of Connes *et al.* We have used the following expression for the rotational energy levels of a non-rigid rotator (the energy levels of a rigid rotator are given by Equation (18)):

$$E_{\text{rot}}(J) = hc(B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \dots)$$

For most vibrational levels the constant H_v was taken to be equal to zero. The rotational line positions are given by

$$\omega(m) = \omega_0 + am + bm^2 + cm^3 + dm^4 + \dots,$$

where

$$\begin{aligned} a &= (B' + B''), \\ b &= (B' - B'') - (D' - D''), \\ c &= -2(D' + D''), \end{aligned}$$

and

$$d = -(D' - D'');$$

double primes refer to the lower vibrational state and primes to the upper vibrational state. The index $m = J'' + 1$ for the *R* branch and $m = -J''$ for the *P* branch. The rotational constants for the ground state of the ¹²C¹⁶O₂ isotope are accurately known: $B(00^0) = 0.390218 \text{ cm}^{-1}$ and $D(00^0) = 13.3 \times 10^{-8} \text{ cm}^{-1}$. The vibrational energy levels are identified by the vibrational quantum numbers $v_1 v_2 v_3$.

Many isotopic bands of carbon dioxide can be seen in the spectrum of Venus, and we will use the following notation for the isotopes: $626 = {}^{12}\text{C}^{16}\text{O}_2$, $636 = {}^{13}\text{C}^{16}\text{O}_2$, $628 = {}^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $627 = {}^{12}\text{C}^{16}\text{O}^{17}\text{O}$, $638 = {}^{13}\text{C}^{16}\text{O}^{18}\text{O}$, etc.

The rotational line intensities, $S(J)$ or $S(m)$, are found from Equation (15). The factor $F(J)$, or $F(m)$, is given by Herzberg (1950): For parallel bands, $l' = l''$, we have

$$F(m) = (m^2 - l^2)/m$$

for the *P* and *R* branches ($J' = J'' - 1$ and $J' = J'' + 1$, respectively);

$$F(J) = l^2(2J'' + 1)/(J''(J'' + 1))$$

TABLE B-I
Rotational constants for different lower vibrational states

(a) Nonsymmetrical molecules of CO ₂			
Vibrational state	example	Rotational constant	Rotational quantum number
Σ	00 ⁰ 0	B^c	$J = 0, 1, 2, 3, 4, \dots$
Π	01 ¹ 0	B^c	$J = 1, 2, 3, 4, 5, \dots$
		B^d	$J = 1, 2, 3, 4, 5, \dots$
Δ	02 ² 0	B^c	$J = 2, 3, 4, 5, 6, \dots$
		B^d	$J = 2, 3, 4, 5, 6, \dots$

(b) Symmetrical molecules of CO ₂			
Σ_g	00 ⁰ 0	B^c	$J = 0, 2, 4, 6, 8, \dots$
Σ_u	00 ⁰ 1	B^c	$J = 1, 3, 5, 7, 9, \dots$
		B^d	$J = 1, 3, 5, 7, 9, \dots$
Π_u	01 ¹ 0	B^c	$J = 2, 4, 6, 8, 10, \dots$
		B^d	$J = 2, 4, 6, 8, 10, \dots$
Δ_g	02 ² 0	B^c	$J = 3, 5, 7, 9, 11, \dots$
		B^d	$J = 3, 5, 7, 9, 11, \dots$

TABLE B-II
Absorption intensity units

Units for (path × concentration)	Units for intensity, S (frequency/length × concentration)
1.0 cm atm _{300 K} = 0.91 cm atm _{stp}	1.0 cm ⁻¹ /cm atm _{stp} = 0.91 cm ⁻¹ /cm atm _{300 K}
1.0 cm atm _{296 K} = 0.922 cm atm _{stp}	1.0 cm ⁻¹ /cm atm _{stp} = 0.922 cm ⁻¹ /cm atm _{296 K}
1.0 km atm _{stp} = 10 ⁵ cm atm _{stp}	1.0 cm ⁻¹ /cm atm _{stp} = 10 ⁵ cm ⁻¹ /km atm _{stp}
1.0 mole/cm ² = 22.415 cm atm _{stp}	1.0 cm ⁻¹ /cm atm _{stp} = 22,415 cm/mole
1.0 mole/cm ² = 0.24303 km atm _{296 K}	1.0 cm ⁻¹ /km atm _{296 K} = 0.24303 cm/mole
1.0 cm atm _{stp} = 2.69 × 10 ¹⁹ molecules cm ⁻²	1.0 cm/molecule = 2.69 × 10 ¹⁹ cm ⁻¹ /cm atm _{stp}
1.0 km atm _{296 K} = 2.48 × 10 ²⁴ molecules cm ⁻²	1.0 cm/molecule = 2.48 × 10 ²⁴ cm ⁻¹ /km atm _{296 K}
	1 'intensity unit' = 10 ⁷ cm/mole
	1 'intensity unit' = 446 cm ⁻¹ /cm atm _{stp}
	1.0 cm ⁻¹ /cm atm _{stp} = 30 GHz/cm atm _{stp}

Relationships between integrated intensity and transition probabilities at 273.16K

Electric dipole matrix element, $\langle M \rangle$ (Debye or 10 ⁻¹⁸ esu)	$S = 11.1908 \omega \langle M \rangle^2 (273/T) (N_1/N)$
f -number (dimensionless)	$S = 2.3789 \times 10^7 f (273/T) (N_1/N)$
Einstein absorption coefficient, B (sg ⁻¹)	$S = 1.7801 \times 10^7 \omega B (273/T) (N_1/N)$
Einstein emission coefficient, A (s ⁻¹)	$S = 3.5670 \times 10^7 \omega^{-2} A (273/T) (N_1/N)$

Here S has the units cm⁻¹/cm atm_T, ω is the wavenumber of the band in cm⁻¹ and (N_1/N) is the fraction of the molecules in the lower energy state.

TABLE B-III
Carbon dioxide bands in the Connes *et al.* (1969) infrared spectra of Venus

Band origin ω_0 cm ⁻¹ (in vacuum)	Rotational Constants			Isotope	Transition	Branch	Intensity S_r cm ⁻¹ /km atm ₂₉₆ K	Interaction term, ζ_r
	$a \times 10^3$ (cm ⁻¹)	$b \times 10^3$	$c \times 10^8$					
3980.60	77621.3	-711.7	-53.6	626	01 ¹ 2-02 ² 0	Rc	0.05	+0.1
3980.60	77681.3	-651.7	-55.8	626	01 ¹ 2-02 ² 0	Rd	0.05	+0.1
3980.60	-651.7	-651.7	-1.4	626	01 ¹ 2-02 ² 0	Qc	0.05	+0.1
3980.60	-711.7	-711.7	0.8	626	01 ¹ 2-02 ² 0	Qd	0.05	+0.1
3987.61	73633.0	1.0	-40.4	628	(30 ⁰ -00 ⁰) _{II}	Rc	4.0	0
4005.94	-719.0	-719.0	0.4	626	00 ⁰ 2-01 ¹ 0	Qd	2.0	+0.12
4005.94	77469.0	-658.0	-52.8	626	00 ⁰ 2-01 ¹ 0	Rc	2.0	+0.12
4023.48	75698.0	-30.0	-48.0	627	(30 ⁰ -00 ⁰) _{II}	Rc	0.2	0
4030.32	77503.2	-593.6	-57.4	626	(01 ¹ 2-10 ⁰) _{II}	Rc	0.05	+0.1
4030.32	-533.6	-533.6	2.4	628	(01 ¹ 2-10 ⁰) _{II}	Qc	0.05	+0.1
4167.91	73508.0	125.0	-36.0	628	(30 ⁰ -00 ⁰) _I	Rc	0.03	0
4416.150	78157.5	113.9	-61.0	626	(31 ⁰ -00 ⁰) _{IV}	Rc	0.1	+0.15
4416.150	286.0	286.0	-6.0	626	(31 ⁰ -00 ⁰) _{IV}	Qc	0.1	+0.15
4508.749	73078.0	-557.8	-44.4	638	00 ⁰ 2-00 ⁰	Rc	0.4	0
4524.88	75155.0	-577.0	-48.2	637	00 ⁰ 2-00 ⁰	Rc	0.04	0
4529.870	77985.5	-58.1	-63.4	626	(40 ⁰ -01 ¹ 0) _{IV}	Rc	0.01	+0.2
4529.870	-119.1	-119.1	-10.6	626	(40 ⁰ -01 ¹ 0) _{IV}	Qd	0.01	+0.2
4578.09	78214.0	85.5	-52.8	626	(32 ⁰ -01 ¹ 0) _{III}	Rc	0.01	+0.2
4578.09	78275.0	24.5	-56.8	626	(32 ⁰ -01 ¹ 0) _{III}	Rd	0.01	+0.2
4578.09	85.5	85.5	-3.6	626	(32 ⁰ -01 ¹ 0) _{III}	Qc	0.01	+0.2,
4578.09	24.5	24.5	0.4	626	(32 ⁰ -01 ¹ 0) _{III}	Qd	0.01	+0.2,
4591.118	78014.3	-29.3	-56.4	626	(31 ⁰ -00 ⁰) _{III}	Rc	0.25	+0.18
4591.118	112.0	112.0	-3.0	626	(31 ⁰ -00 ⁰) _{III}	Qc	0.25	+0.18
4611.31	77836.0	-186.5	-59.4	626	(31 ¹ -11 ¹ 0) _{IV} ¹	Rc	0.05	0
4611.31	78162.0	-113.0	-62.2	626	(31 ¹ -11 ¹ 0) _{IV} ¹	Rd	0.05	0
4614.779	73132.0	-574.0	-43.8	628	01 ¹ 2-01 ¹ 0	Rc	1.4	0
4614.779	73240.8	-577.2	-43.8	628	01 ¹ 2-01 ¹ 0	Rd	1.4	0
4630.37	75217.0	-591.0	-48.0	627	01 ¹ 2-01 ¹ 0	Rc	0.13	0
4630.37	75330.0	-594.0	-48.0	627	01 ¹ 2-01 ¹ 0	Rd	0.13	0
4639.502	73053.6	-579.2	-44.4	628	00 ⁰ 2-00 ⁰	Rc	35.0	0
4655.205	75131.5	-596.7	-48.2	627	00 ⁰ 2-00 ⁰	Rc	3.4	0
4673.68	78154.0	-169.0	-56.0	636	(22 ² 1-02 ² 0) _{III}	Rc	0.2	0
4673.68	78154.0	-169.0	-60.0	636	(22 ² 1-02 ² 0) _{III}	Rd	0.2	0

4683.12	77048.0	-99.0	-52.0	0	636	(3110-0000)H	Rc	0.005	+0.2
4685.77	73057.7	-126.5	-78.2	-8.5	636	(3091-1090)IV ¹¹	Rc	0.5	0
4687.798	77909.4	-132.4	-64.4	-7.6	626	(3091-1090)IV ¹	Rc	0.90	0
4692.18	73468.0	-168.0	-52.4	-4.0	638	(2091-0090)III	Rc	0.7	0
4708.52	77924.4	-198.4	-56.6	-1.7	636	(2111-0110)III	Rc	4.0	0
4708.52	78135.6	-112.8	-60.2	-3.5	636	(2111-0110)III	Rd	4.0	0
4718.35	75567.0	-165.0	-54.0	-3.0	637	(2091-0090)III	Rc	0.1	0
4721.92	69103.0	-282.0	-41.6	0.0	828	(2091-0090)III	Rc	0.25	0
4732.90	78275.0	-201.0	-63.0	-4.0	626	(2331-0330)III	Rcd	1.8	0
4743.70	73436.5	-269.5	-50.8	-3.0	628	(2111-0110)III	Rc	4.5	0
4743.70	73596.0	-222.0	-46.8	-1.0	628	(2111-0110)III	Rd	4.5	0
4748.05	77907.0	-140.0	-61.8	-4.7	636	(2091-0090)III	Rc	72.0	0
4753.41	77993.0	-51.0	-48.2	1.6	626	(3110-0090)H	Rc	0.3	+0.30
4753.41	88.0	88.0	0.0	0	626	(3110-0090)H	Qc	0.3	+0.30
4757.705	77928.0	-218.4	-62.2	-3.1	626	(3111-1110)IV ¹¹	Rc	4.8	0
4757.705	78192.0	-143.6	-64.6	-3.7	626	(3111-1110)IV ¹¹	Rd	4.8	0
4768.54	78103.0	-224.0	-52.8	1.0	626	(2221-0220)III	Rc	35.0	0
4768.54	78109.0	-224.0	-60.0	-3.0	626	(2221-0220)III	Rd	35.0	0
4784.66	77242.0	-194.0	-60.4	-4.0	626	(2092-0091)III	Rc	0.4	0
4786.688	77734.9	-347.3	-54.0	-1.8	626	(3111-1110)III ¹	Rc	1.6	0
4786.688	77970.6	-304.0	-55.4	-1.5	626	(3111-1110)III ¹	Rd	1.6	0
4790.573	77936.9	-159.9	-71.0	-4.3	626	(3091-1090)IV ¹¹	Rc	42.0	0
4791.26	73388.0	-243.0	-52.2	-3.9	628	(2091-0090)III	Rc	126.0	0
4807.692	78067.6	-183.0	-60.2	-3.5	626	(2111-0110)III	Rd	900.0	0
4807.692	77879.0	-250.0	-53.0	0	626	(2111-0110)III	Rc	900.0	0
4808.186	78073.0	-56.0	-46.0	3.6	626	(4090-0110)H	Rc	~0	0
4808.186	-117.0	-117.0	7.0	3.6	626	(4090-0110)H	Qd	~0	0
4814.57	73299.0	-337.0	-44.4	0	638	(2091-0090)H	Rc	3.6	0
4821.50	75505.0	-223.0	-56.0	-4.0	627	(2091-0090)III	Rc	20.0	0
4839.731	77692.0	-349.8	-57.6	-4.2	626	(3091-1090)III ¹	Rc	37.0	0
4853.62	77841.0	-203.0	-61.2	-4.4	626	(2091-0090)III	Rc	21700.0	0
4871.46	77767.0	-356.0	-49.8	1.7	636	(2111-0110)H	Rc	32.0	0
4871.46	77945.0	-303.0	-52.6	0.3	636	(2111-0110)H	Rd	32.0	0
4887.39	77708.0	-339.0	-55.2	-1.4	636	(2091-0090)H	Rc	800.0	0
4887.97	77918.0	-126.0	-52.4	0	626	(1221-0090)H	Rc	2.2 × 10 ⁻³	...
4896.185	73379.0	-327.0	-45.0	0	628	(2111-0110)H	Rc	12.0	0
4896.185	73530.0	-288.0	-45.0	0	628	(2111-0110)H	Rd	12.0	0
4904.85	73301.0	-332.0	-44.4	0	628	(2091-0090)H	Rc	300.0	0
4924.98	73366.0	-270.0	-38.4	3.0	638	(2091-0090)H	Rc	1.2	0
4828.91	75464.0	-344.0	-48.0	0	627	(2111-0110)H	Rc	2.0	0

Table B-III (Continued)

Band origin ω_0 cm ⁻¹ (in vacuum)	Rotational Constants		$d \times 10^8$	$c \times 10^8$	Isotope	Transition	Branch	Intensity S_v cm ⁻¹ /km atm _{296 K}	Interaction term, ζ_v
	$a \times 10^5$ (cm ⁻¹)	$b \times 10^5$							
4828.91	75626.0	-298.0	0	-48.0	627	(21 ¹ 1-01 ¹ 0) _{II}	Rd	2.0	0
4931.083	77767.0	-369.2	-0.4	-56.8	626	(31 ¹ 1-11 ¹ 0) _{III} ^{II}	Rc	13.0	0
4931.083	78001.3	-334.7	-0.3	-57.6	626	(31 ¹ 1-11 ¹ 0) _{III} ^{II}	Rd	13.0	0
4939.33	75377.0	-351.0	0	-48.0	627	(20 ⁰ 1-00 ⁰ 0) _{II}	Rc	62.0	0
4942.506	77719.5	-377.3	-0.9	-64.2	626	(30 ⁰ 1-10 ⁰ 0) _{III} ^{II}	Rc	380.0	0
4946.807	77721.0	-361.4	-1.7	-53.8	626	(31 ¹ 1-11 ¹ 0) _{II} ^I	Rc	8.0	0
4946.807	77947.0	-326.8	2.3	-47.4	626	(31 ¹ 1-11 ¹ 0) _{II} ^I	Rd	8.0	0
4953.363	78013.0	-320.0	0.1	-54.6	626	(22 ² 1-02 ² 0) _{II}	Rc	140.0	0
4953.363	78013.0	-320.0	1.2	-51.8	626	(22 ² 1-02 ² 0) _{II}	Rd	140.0	0
4959.668	77666.3	-375.5	2.8	-44.0	626	(30 ⁰ 1-10 ⁰ 0) _{II} ^I	Rc	225.0	0
4965.36	77766.1	-362.5	0.9	-51.4	626	(21 ¹ 1-01 ¹ 0) _{II}	Rc	3570.0	0
4965.36	77938.1	-312.5	0.4	-52.4	626	(21 ¹ 1-01 ¹ 0) _{II}	Rd	3570.0	0
4977.83	77674.5	-369.1	0.2	-52.0	626	(20 ⁰ 1-00 ⁰ 0) _{II}	Rc	94000.0	0
4991.35	77694.0	-353.5	3.9	-44.6	636	(20 ⁰ 1-00 ⁰ 0) _I	Rc	570.0	0
5013.783	77746.7	-376.1	2.3	-48.6	636	(21 ¹ 1-01 ¹ 0) _I	Rc	23.0	0
5013.783	77918.6	-329.8	3.3	-46.6	636	(21 ¹ 1-01 ¹ 0) _I	Rd	23.0	0
5028.78	77836.0	-350.0	-0.2	-56.0	636	(22 ² 1-02 ² 0) _I	Rc	0.4	0
5028.78	77836.0	-350.0	2.3	-49.4	636	(22 ² 1-02 ² 0) _I	Rd	0.4	0
5042.58	73429.0	-204.0	2.5	-39.4	628	(20 ⁰ 1-00 ⁰ 0) _I	Rc	61.0	0
5061.776	77873.0	-171.0	0.5	-51.4	626	(12 ² 1-00 ⁰ 0) _I	Rc	2.5 × 10 ⁻⁵	...
5062.443	77693.8	-403.0	6.1	-50.2	626	(30 ⁰ 1-10 ⁰ 0) _{III} ^{II}	Rc	64.0	0
5064.68	73442.0	-264.0	0	-45.0	628	(21 ¹ 1-01 ¹ 0) _I	Rc	3.5	0
5064.68	73619.0	-199.0	3.0	-39.0	628	(21 ¹ 1-01 ¹ 0) _I	Rd	3.5	0
5068.93	75496.0	-232.0	2.0	-44.0	627	(20 ⁰ 1-00 ⁰ 0) _I	Rc	17.0	0
5099.66	77770.6	-273.0	4.1	-44.2	626	(20 ⁰ 1-00 ⁰ 0) _I	Rc	30200.0	0
5114.892	77819.7	-222.0	4.8	-39.6	626	(30 ⁰ 1-10 ⁰ 0) _I ^I	Rc	83.0	0
5123.20	77806.0	-323.0	2.3	-48.6	626	(21 ¹ 1-01 ¹ 0) _I	Rc	1430.0	0
5123.20	77987.0	-264.0	3.3	-46.6	626	(21 ¹ 1-01 ¹ 0) _I	Rd	1430.0	0
5139.40	78032.0	-301.0	-1.4	-57.6	626	(22 ² 1-02 ² 0) _I	Rc	55.0	0
5139.40	78032.0	-301.0	1.6	-50.8	626	(22 ² 1-02 ² 0) _I	Rd	55.0	0
5168.60	77493.0	-554.0	0	-52.4	636	01 ¹ 2-00 ⁰ 0	Rc	0.5	0
5168.60	-493.0	-493.0	0	0	636	01 ¹ 2-00 ⁰ 0	Rc	0.5	0
5217.667	77847.0	-249.6	8.1	-46.2	626	(30 ⁰ 1-10 ⁰ 0) _{II} ^{II}	Qc	6.3	0
5584.391	77119.0	-922.0	-0.8	-50.8	626	(00 ⁰ 3-10 ⁰ 0) _I	Rc	1.9	0

5670.08	77243.0	-923.0	-55.0	0.5	626	(0113-1110) _{II}	Rc	0	0.02
5670.08	77374.0	-962.0	-55.0	1.0	626	(0113-1110) _{II}	Rd	0	0.02
5687.166	77147.4	-949.4	-57.4	2.5	626	(0093-1090) _{II}	Rc	0	2.0
5830.792	78025.7	-17.9	-61.4	-4.5	626	(4110-0090) _{IV}	Rc	0	0.20
5858.022	73065.4	-567.4	-49.3	-2.47	628	(1092-0070) _{II}	Rc	0	1.04
5885.336	75154.0	-574.0	-48.2	0	627	(1092-0070) _{II}	Rc	0	0.04
5904.47	77959.0	-164.0	-59.	-3.0	636	(3111-0110) _{IV}	Rc	0	0.05
5904.47	78214.0	-34.0	-63.0	-5.0	636	(3111-0110) _{IV}	Rd	0	0.05
5933.8	...	-223.0	628	(3111-0110) _{IV}	Rc	0	0.08
5951.59	77989.0	-58.0	-73.8	-10.7	636	(3091-0090) _{IV}	Rc	0	0.50
5955.8	73000.0	-280.0	628	(1112-0110) _I	Rc	0	0.08
5959.954	73076.9	-555.9	-40.1	2.15	628	(1092-0090) _I	Rc	0	0.95
5972.54	78159.0	-174.0	-47.4	3.6	626	(3291-0290) _{IV}	Rc	0	0.7
5972.54	78159.0	-174.0	-59.2	-2.6	626	(3291-0290) _{IV}	Rd	0	0.7
5987.0	627	(1092-0090) _I	...	0	0.02
5993.581	73450.1	-182.7	-182.7	-6.7	628	(3091-0090) _{IV}	Rc	0	1.0
5998.569	78003.4	-93.4	-77.0	-7.3	626	(4091-1090) _{V^{II}}	Rc	0	1.3
6000.52	77940.0	-104.0	-52.4	0.0	626	(4110-0090) _{III}	Rc	0	0.2
6020.795	77919.0	-209.6	-60.8	-3.8	626	(3111-0110) _{IV}	Rc	0	12.6
6020.795	78139.7	-100.9	-62.6	-4.7	626	(3111-0110) _{IV}	Rd	0	12.6
6027.6	638	(3091-0090) _{III}	...	0	0.1
6033.478	75569.0	-159.0	-60.0	-6.0	627	(3091-0090) _{IV}	Rc	0	0.12
6072.34	77752.0	-289.0	-62.8	-6.8	626	(4091-1090) _{IV^I}	Rc	0	0.2
6075.98	77911.0	-133.0	-66.0	-6.8	626	(3091-0090) _{IV}	Rc	0	128.0
6088.21	77800.0	-323.0	-59.6	-3.0	636	(3111-0110) _{III}	Rc	0	0.6
6088.21	78015.0	-233.0	-58.2	-2.5	636	(3111-0110) _{III}	Rd	0	0.6
6103.67	77967.0	-79.0	-51.6	0.4	626	(2291-0090) _{III}	Rc	0	0.2
6119.61	77783.0	-264.0	-61.6	-4.6	636	(3091-0090) _{III}	Rc	0	8.1
6127.782	73265.9	-366.9	-48.4	-2.0	628	(3091-0090) _{III}	Rc	0	6.8
6170.09	78028.0	-305.0	-51.6	1.6	626	(3291-0290) _{III}	Rc	0	3.6
6170.09	78028.0	-305.0	-53.2	0.4	626	(3291-0290) _{III}	Rd	0	3.6
6175.12	77780.0	-317.0	-69.4	-3.5	626	(4091-1090) _{IV^{II}}	Rc	0	5.0
6175.950	75364.0	-364.0	-52.0	-2.0	627	(3091-0090) _{III}	Rc	0	0.9
6179.01	77986.0	-58.0	-52.4	0	626	(4110-0090) _{II}	Rc	0	0.2
6196.174	77758.2	-370.4	-55.4	-1.1	626	(3111-0110) _{III}	Rc	+	75.0
6196.174	77958.6	-292.0	-55.8	-1.3	626	(3111-0110) _{III}	Rd	0	75.0
6205.60	77577.0	-465.0	-54.8	-2.8	626	(4091-1090) _{III^I}	Rc	0	3.0
6227.91	77689.0	-355.0	-57.4	-2.5	626	(3091-0090) _{III}	Rc	0	1200.0
6241.96	77609.0	-438.0	-47.6	2.4	636	(3091-0090) _{II}	Rc	0	13.0
6243.57	77702.0	-422.0	-53.0	0	636	(3111-0110) _{III}	Rc	0	1.1

Table B-III (Continued)

Band origin ω_0 cm ⁻¹ (in vacuum)	Rotational Constants			Isotope	Transition	Branch	Intensity S_v cm ⁻¹ /km atm ⁻² °K	Interaction term, ζ_r
	$a \times 10^5$ (cm ⁻¹)	$b \times 10^5$	$c \times 10^8$					
6243.57	77895.0	-353.0	-50.0	636	(31 ¹ -01 ⁰) _{II}	Rd	1.1	0
6254.592	73344.0	-259.0	-41.4	628	(30 ⁰ 1-00 ⁰) _{II}	Rc	4.0	0
6288.492	77869.0	-175.0	-53.4	626	(22 ² 1-00 ⁰) _{II}	Rc	0.5	0
6298.07	75404.0	-324.0	-46.2	627	(30 ⁰ 1-00 ⁰) _{II}	Rc	0.8	0
6308.28	77604.0	-493.0	-61.4	626	(40 ⁰ 1-10 ⁰) _{III} ^{II}	Rc	5.3	0
6318.17	77696.0	-450.0	-54.2	626	(41 ¹ -11 ⁰) _{III} ^{II}	Rd	0.5	0
6318.17	77949.0	-387.0	-54.8	626	(41 ¹ -11 ⁰) _{III} ^{II}	Rd	0.5	0
6346.27	77724.0	-318.0	-50.4	626	(40 ⁰ 1-10 ⁰) _{II} ^I	Rc	3.0	0
6347.855	77667.4	-376.4	-45.2	626	(30 ⁰ 1-00 ⁰) _{II}	Rc	1150.0	0
6356.293	77740.9	-387.7	-51.2	626	(31 ¹ -01 ⁰) _{II}	Rc	90.0	0
6356.293	77936.8	-313.8	-48.2	626	(31 ¹ -01 ⁰) _{II}	Rd	90.0	0
6359.32	77814.0	-348.0	-50.6	626	(32 ² 1-02 ²) _{II}	Rc	2.5	0
6359.32	77814.0	-348.0	-49.2	626	(32 ² 1-02 ²) _{II}	Rd	2.5	0
6363.62	77727.0	-320.0	-44.2	636	(30 ⁰ 1-00 ⁰) _I	Rc	3.5	0
6388.085	78050.8	7.2	-44.4	626	(41 ⁰ -00 ⁰) _I	Rc	6.0	+0.005
6397.545	77749.0	-374.0	-51.0	636	(31 ¹ -01 ⁰) _I	Rc	0.2	0
6397.545	77948.0	-300.0	-45.0	636	(31 ¹ -01 ⁰) _I	Rd	0.2	0
6429.172	73478.0	-154.8	-34.2	628	(30 ⁰ 1-00 ⁰) _I	Rc	0.3	0
6449.05	77751.0	-346.0	-56.2	626	(40 ⁰ 1-10 ⁰) _{II} ^{II}	Rc	0.01	0
6463.48	75542.0	-186.0	-32.0	627	(30 ⁰ 1-00 ⁰) _I	Rc	0.1	0
6466.44	77593.0	-535.5	-61.2	626	(20 ² -01 ⁰) _{III}	Rc	0.4	+0.03
6466.44	-595.5	-595.5	-8.0	626	(20 ² -01 ⁰) _{III}	Qd	0.4	+0.03
6474.53	77888.0	-156.0	-56.2	626	(22 ² 1-00 ⁰) _I	Rc	0.4	0
6498.67	77666.0	-462.0	...	626	(12 ² -01 ⁰) _{II}	Rc	0.6	+0.02
6498.67	77727.0	-523.0	...	626	(12 ² -01 ⁰) _{II}	Rd	0.6	+0.02
6498.67	-462.0	-462.0	...	626	(12 ² -01 ⁰) _{II}	Qc	0.6	+0.02
6498.67	-523.0	-523.0	4.0	626	(12 ² -01 ⁰) _{II}	Qd	0.6	+0.02
6503.079	77820.6	-223.0	-41.2	626	(30 ⁰ 1-00 ⁰) _I	Rc	135.0	0
6532.65	77877.0	-165.0	-36.2	626	(40 ⁰ 1-10 ⁰) _I ^I	Rc	0.1	0
6536.45	77825.0	-307.0	-47.2	626	(31 ¹ -01 ⁰) _I	Rc	13.0	0
6536.45	78039.0	-212.0	-43.2	626	(31 ¹ -01 ⁰) _I	Rd	13.0	0
6537.958	...	-542.4	-51.6	626	(11 ² -00 ⁰) _{II}	Rc	6.0	+0.005
6537.958	-449.6	-449.6	-5.02	626	(11 ² -00 ⁰) _{II}	Qc	6.0	+0.005
6562.444	78058.0	-275.0	...	626	(32 ² 1-02 ²) ₀	Rc	0.7	0

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6562.444	78056.0	-277.0	...	626	(32 ² 1-02 ² 0)	Rd	0.7	0
6635.43	77904.0	-192.5	42.8	626	(40 ² 1-10 ² 0) _I ^{II}	Rc	0.05	0
6670.77	77613.0	-515.0	-52.8	626	(12 ² 2-01 ¹ 0) _I	Rc	0.7	+0.03
6670.77	77674.0	-576.0	-52.8	626	(12 ² 2-01 ¹ 0) _I	Rd	0.7	+0.03
6670.77	-515.0	-515.0	1.4	626	(12 ² 2-01 ¹ 0) _I	Qc	0.7	+0.03
6670.77	-576.0	-576.0	0.4	626	(12 ² 2-01 ¹ 0) _I	Qd	0.7	+0.03
6679.709	77452.8	-590.8	-50.1	626	(11 ² 2-00 ² 0) _I	Rc	8.0	+0.01
6679.709	...	-509.1	...	626	(11 ² 2-00 ² 0) _I	Rc	8.0	+0.01
6710.32	77505.0	-624.0	-51.2	626	(20 ² 2-01 ¹ 0) _I	Qc	0.2	0
6710.32	-685.0	-685.0	2.0	626	(20 ² 2-01 ¹ 0) _I	Qd	0.2	0
6728.36	72800.0	-837.0	-44.4	638	00 ² 3-00 ² 0	Rc	0.2	0
6745.12	7243.3	-879.5	-53.2	636	01 ¹ 3-01 ¹ 0	Rc	3.5	0
6745.12	77363.9	-884.5	-53.2	636	01 ¹ 3-01 ¹ 0	Rd	3.5	0
6780.215	77160.0	-887.0	-53.4	636	00 ² 3-00 ² 0	Rc	44.0	0
6804.404	77177.0	-864.8	-55.7	626	(10 ² 3-10 ² 0) _{II} ^I	Rc	...	0
6867.281	77167.6	-904.8	-48.8	626	(11 ¹ 3-11 ¹ 0) _I ^I	Rc	0.6	0
6867.281	77340.7	-933.9	-49.4	626	(11 ¹ 3-11 ¹ 0) _I ^I	Rd	0.6	0
6870.795	77259.9	-886.3	-55.3	626	(11 ¹ 3-11 ¹ 0) _{II} ^I	Rc	0.3	0
6870.795	77442.4	-893.6	-58.2	626	(11 ¹ 3-11 ¹ 0) _{II} ^I	Rd	0.3	0
6897.751	77426.5	-905.5	-56.2	626	02 ² 3-02 ² 0	Rcd	11.0	0
6897.80	76505.0	-920.0	-53.2	626	00 ² 4-00 ² 1	Rc	0.18	0
6905.770	77101.4	-940.4	-46.7	626	(10 ² 3-10 ² 0) _I ^I	Rc	5.0	0
6907.144	77204.5	-892.3	-62.3	626	(10 ² 3-10 ² 0) _{II} ^{II}	Rc	7.0	0
6922.21	72764.3	-868.5	-44.4	628	00 ² 3-00 ² 0	Rc	15.0	0
6935.15	77214.6	-914.0	-53.6	626	01 ¹ 3-01 ¹ 0	Rc	310.0	0
6935.15	77331.6	-919.0	-53.2	626	01 ¹ 3-01 ¹ 0	Rd	310.0	0
6945.0	...	-48.2	-48.2	627	00 ² 3-00 ² 0	Rc	2.0	0
6972.578	77120.8	-922.8	-52.4	626	00 ² 3-00 ² 0	Rc	4000.0	0
7460.53	77754.0	-290.0	-64.4	626	(40 ² 1-00 ² 0) _{IV}	Rc	12.0	0
7481.51	77567.0	-480.0	-32.0	636	(40 ² 1-00 ² 0) _{III}	Rc	0.3	0
7583.265	77688.0	-441.0	-53.2	626	(41 ¹ 1-01 ¹ 0) _{III}	Rc	2.5	0
7583.265	77907.0	-344.0	-53.2	626	(41 ¹ 1-01 ¹ 0) _{III}	Rd	2.5	0
7593.69	77578.0	-466.0	-56.4	626	(40 ² 1-00 ² 0) _{III}	Rc	34.0	0
7600.13	77609.0	-438.0	-38.4	626	(40 ² 1-00 ² 0) _{II}	Rc	0.2	0
7616.62	77975.0	-69.0	-43.2	626	(51 ¹ 0-00 ² 0) _{II}	Rc	0.05	+
7734.46	77725.0	-319.0	-51.2	626	(40 ² 1-00 ² 0) _{II}	Rc	9.0	0
7743.70	77551.0	-493.0	-50.0	626	(21 ¹ 2-00 ² 0) _{III}	Rc	0.6	+0.03
7743.70	-373.0	-373.0	-4.0	626	(21 ¹ 2-00 ² 0) _{III}	Qc	0.6	+0.03
7757.626	77789.0	-339.5	-40.0	626	(41 ¹ 1-01 ¹ 0) _{II}	Rc	0.8	0
7757.626	77978.0	-272.5	-45.4	626	(41 ¹ 1-01 ¹ 0) _{II}	Rd	0.8	0

Table B-III (Continued)

Band origin ω_0 cm ⁻¹ (in vacuum)	Rotational Constants $a \times 10^5$ (cm ⁻¹)	$b \times 10^5$	$c \times 10^8$	$d \times 10^8$	Isotope	Transition	Branch	Intensity S_b cm ⁻¹ /km atm ² 96 K	Interaction term, ζ_b
7897.573	...	-132.0	626	(32 ² 1-00 ⁰) _I	Qc	0.1	0
7901.479	77418.0	-626.0	626	(21 ² -00 ⁰) _{II}	Rc	0.7	+0.015
7901.479	-514.0	-514.0	626	(21 ² -00 ⁰) _{II}	Qc	0.7	+0.015
7920.84	77878.0	-166.0	626	(40 ¹ -00 ⁰) _I	Rc	0.6	0
7929.92	77302.0	-821.0	-37.8	7.3	636	(11 ³ -01 ⁰) _{II}	Rc	0.05	0
7929.92	77460.0	-798.0	-55.0	-1.0	636	(11 ³ -01 ⁰) _{II}	Rd	0.05	0
7961.29	77892.0	-236.0	-57.0	-2.0	626	(41 ¹ -01 ⁰) _I	Rc	0.06	0
7961.29	78104.0	-146.0	-46.0	3.0	626	(41 ¹ -01 ⁰) _I	Rd	0.06	0
7981.29	77251.0	-796.0	-44.0	4.0	626	(10 ³ -00 ⁰) _{II}	Rc	0.8	0
8000.80	77257.0	-785.0	-56.2	-1.9	636	(10 ³ -00 ⁰) _{II}	Rc	0.006	0
8056.024	77463.0	-581.0	-58.8	-4.8	626	(20 ³ -10 ⁰) _{III} ^I	Rc	0.6	0
8056.024	-469.3	-469.3	-48.0	2.2	626	(21 ² -00 ⁰) _I	Qc	0.6	+0.01
8070.91	77190.0	-933.0	5.0	2.5	626	(21 ² -00 ⁰) _I	Rc	0.6	+0.01
8070.91	77324.0	-924.0	-52.0	0.5	636	(11 ³ -01 ⁰) _I	Rc	0.15	0
8084.06	77472.0	-861.0	-53.0	0.0	636	(11 ³ -01 ⁰) _I	Rd	0.15	0
8084.06	-50.8	2.0	626	(12 ³ -02 ⁰) _{II}	Rc	0.3	0
8089.04	77097.0	-950.0	-53.2	0.4	626	(12 ³ -02 ⁰) _{II}	Rd	0.3	0
8103.58	77284.0	-812.0	-51.0	0.7	636	(10 ³ -00 ⁰) _I	Rc	1.9	0
8120.104	72785.0	-848.0	-65.4	0.7	626	(20 ³ -10 ⁰) _{III} ^{II}	Rc	0.4	0
8128.78	77069.0	-973.0	-47.4	-1.5	628	(10 ³ -00 ⁰) _I	Rc	0.52	0
8135.886	77251.1	-877.5	-52.8	-1.8	626	(20 ³ -10 ⁰) _{II} ^I	Rc	0.2	0
8135.886	77399.7	-850.9	-53.9	-0.36	626	(11 ³ -01 ⁰) _{II}	Rc	10.0	0
8154.47	74870.0	-858.0	-57.0	-1.89	627	(11 ³ -01 ⁰) _{II}	Rd	10.0	0
8192.556	77187.0	-865.7	-44.0	2.0	626	(10 ³ -00 ⁰) _{II}	Rc	0.1	0
8220.363	72782.0	-850.8	-57.3	-2.44	626	(10 ³ -00 ⁰) _{II}	Rc	114.0	0
8231.56	77096.0	-1000.0	-41.4	1.5	628	(10 ³ -00 ⁰) _I	Rc	0.52	0
8243.16	77148.0	-894.0	-59.4	1.5	626	(20 ³ -10 ⁰) _{II} ^{II}	Rc	0.3	0
8254.80	77412.0	-921.0	-47.0	1.0	626	(20 ³ -10 ⁰) _I ^I	Rc	0.2	0
8254.80	-54.8	0	626	(12 ³ -02 ⁰) _I	Rc	0.5	0
8255.39	74835.0	-893.0	-52.0	1.0	626	(12 ³ -02 ⁰) _I	Rd	0.5	0
8276.767	77190.7	-937.9	-44.0	2.0	627	(10 ³ -00 ⁰) _I	Rc	0.1	0
8276.767	77328.7	-921.9	-50.2	1.5	626	(11 ³ -01 ⁰) _I	Rc	17.0	0
8293.955	77101.0	-942.2	-49.8	1.7	626	(11 ³ -01 ⁰) _I	Rd	17.0	0
8293.955	-47.4	2.5	626	(10 ³ -00 ⁰) _I	Rc	165.0	0

for the Q branch ($J' = J''$). The isotopes 626 and 636 are symmetrical linear molecules; isotopes like 638 and 627 are non-symmetrical linear molecules. The symmetry, or lack thereof, has the following practical result that some rotational levels are forbidden for the symmetrical molecules and they are allowed for the unsymmetrical molecules. The allowed rotational levels and hence the vibration-rotation transitions which are allowed, by the selection rules, depend on the vibrational state of the molecule. It is discussed in detail by Herzberg (1945) and we will not repeat that material here. We simply mention it for the benefit of the reader who may not be familiar with molecular spectra. The bands of the symmetrical molecules, whose lower state is the vibrational ground state, only have lines for even values of the rotational quantum number, e.g. $R(4)$, $R(6)$, $R(8)$; alternate lines are missing from the spectrum. For the non-symmetrical isotopes, all the lines will be present in the spectrum, e.g. $R(4)$, $R(5)$, $R(6)$. Various tables are available for the carbon dioxide molecule which permit the intensity of a rotational line to be found directly from the band intensity. For example, Gray (1965) has tabulated relative line intensities, $S^0(J)/S^0(v)$, for the 626 molecule at 300 K for all the allowed transitions from the ground state and the first excited state (01^10). These are applicable to laboratory data measured at room temperature. Gray (1967) has also tabulated relative line intensities for the 626 molecule for the temperature range 160 K to 280 K at intervals of 20 K, for ground state (00^00) transitions. Young (1970) gives relative line intensities for the 636, 628, 627, and 638 molecules at 200 K, 250 K and 300 K, for ground state transitions.

For approximate intensity calculations, the rotational partition function, $Q_{\text{rot}}(T)$, (which appears in Equation (15) for the line intensity) can be assumed to be given by the expression for a rigid rotator:

$$Q_{\text{rot}}(T) = (kT/hcB'')(1/s),$$

where s is the symmetry number of the molecule ($s=2$ for 626 and 636; $s=1$ for 627, 628 and 638). Gray and Young (1969) have tabulated internal partition functions for the isotopes of CO_2 from 180 K to 300 K at intervals of 10 K; the 626 isotope has the internal partition functions tabulated from 180 K to 1230 K at intervals of 10 K.

The vibrational energy states are called Σ , Π , Δ , Φ , ... states for values of the vibrational angular momentum $l=0, 1, 2, 3, \dots$. All vibrational states are doubly degenerate for $l \neq 0$, since there are two equivalent directions for the vibrational angular momentum vector l . This causes each rotational level to be split into two components; they are separated by an energy difference

$$\delta E(J) = hc(qJ(J+1) - \mu J^2(J+1)^2),$$

where $q = B^d - B^c$ and $\mu = D^d - D^c$. For many rotational levels the splitting may be so slight that $B^d = B^c$ for all practical purposes. The vibrational energy states of symmetrical molecules (626, etc.) have an additional label which refers to the behavior of the eigenfunctions with respect to the operation of inversion. A subscript g indicates that the eigenfunctions are symmetric and a subscript u indicates that they are anti-

symmetric. These subscripts tell us whether B^d or B^c is the appropriate constant to use for a particular rotational line. For the unsymmetrical isotopes (e.g. 628) Table B-Ia summarizes the rules for using B^d and B^c . Table B-Ib gives the rules for symmetrical isotopes (e.g. 626): not all possible states are listed, but all of the lower vibrational states giving rise to bands in the spectrum of Venus are included.

We have attempted to limit the theoretical discussion to a minimum and still provide some explanation of the quantities that are tabulated. The last quantity which we shall mention is the constant ζ_v . A vibration-rotation interaction occurs for some bands and it causes the rotational intensity distribution to be modified by a factor $(1 + \zeta_v m)^2$. We denote the unperturbed line intensity by $S^0(m)$ and the perturbed line intensity by $S_v(m)$ where $S_v(m) = S^0(m) [1 + m\zeta_v]^2$.

In Equation (16) we defined the band intensity $S(v)$ as the sum of the individual line intensities. For bands with no Coriolis interaction, i.e. $\zeta_v = 0$, this definition still applies:

$$S^0(v) = \sum_{\omega} S^0(m).$$

However for bands with a vibration-rotation interaction, it is convenient to use this same definition of band intensity even though it is not the actual band intensity, $S_v(v) = \sum_m S_v(m)$. We have tabulated $S^0(v)$ in units of cm^{-1} per km atm of carbon dioxide at a pressure of 1 atm and a temperature of 296 K (room temperature).

We give some conversion factors for various units which have been used to report band intensities in Table B-II. These may be used to convert our measurements to other systems of units.

DISCUSSION

Traub: Doppler shift measurements in the 8700 Å CO_2 band have been made on a number of occasions by N. P. Carleton and myself. The result is that on most days for which we have good data, the equatorial wind speed appears to be near 100 m s^{-1} , retrograde, with errors of the order of 10 m s^{-1} . The same speed has been measured by us for a Fraunhofer line, indicating that both the visible clouds, and the CO_2 gas participate in this rotation.

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