Reports

Venus Clouds: Structure and Composition

Abstract. The clouds of Venus consist of a fine sulfuric acid aerosol similar to that found in the earth's stratosphere. The acid aerosol on Venus appears to be uniformly mixed with the gas, at least in the visible layers, and possibly down to the cloud base.

Aqueous H_2SO_4 solutions of high concentration have recently been shown (1-4) to explain the refractive index and infrared spectrum of the clouds of Venus, and to account for the extreme dryness of the stratosphere of that planet. The acid forms by the hydration of SO₃, which is readily produced photochemically (1-5) from other sulfur-containing gases. Similar aerosols occur in the earth's stratosphere (6, 7).

There has been disagreement about the concentration of H_2SO_4 required to explain the Venus clouds. Sill (1) originally proposed 86 percent (by weight) acid, whereas Young and Young (2) have suggested that 76 percent acid fits the data best. New data (7) on 75 and 90 percent H_2SO_4 allow this problem to be examined more closely.

Figure 1 shows the spectral extinction coefficients of 75 and 90 percent H_2SO_4 aerosols (7). These were calculated for a size distribution typical of the earth's stratosphere; the average size is a little smaller than is typical for the Venus cloud droplets. However, as the particle size for both planets is small by comparison with the wavelength (~10 μ m) in this spectral region, the exact size distribution affects only the magnitude of the extinction

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coefficient, not its spectral variation. Therefore, the data of Fig. 1 can be applied to Venus.

Figure 2 shows spectra of Venus for the same wavelength region. The lowresolution spectra of Hanel *et al.* (8) and Gillett *et al.* (9) cover a broader spectral range than recent high-resolution spectra (10), which extend only from 750 to 1000 cm⁻¹. In this region, it is possible to estimate the continuum level within CO₂ bands; the continuum, which is attributable to the clouds' thermal emission, is what is needed here. Such estimated parts of the continuum are shown with dashed lines in Fig. 2.

However, in view of the fact that Hanel *et al.* (10) give only the ratio of Venus to the moon rather than the brightness temperature, the low-resolution spectra (8, 9) have similarly been reduced to ratios for comparison. The lunar spectrum of Hanel *et al.* (8) is (apart from noise) indistinguishable from a 256°K blackbody; Fig. 2 shows the ratio of their Venus data to such a mean lunar blackbody curve. The brightness temperatures of Gillett *et al.*



Fig. 1. Spectral extinction coefficients of 75 percent (solid line) and 90 percent (broken line) H_2SO_4 aerosols, according to Remsberg (7).

(9) are systematically lower than those of Hanel *et al.* (8); I have plotted in Fig. 2 the ratio of the Venus data to the 225° K blackbody curve given by Gillett *et al.* (9).

As these data are on the high-frequency side of the Planck function, the Wien approximation can be used to show that

$$\frac{F(T_{1},\nu)}{F(T_{2},\nu)} \approx \exp\left[\frac{A\nu(T_{1}-T_{2})}{T_{1}T_{2}}\right]$$

where A is a constant. Because Fig. 2 is a logarithmic plot of such a flux ratio, it is nearly linear in the temperature difference between the brightness temperature of the Venus clouds (T_1) and the reference blackbody temperature (T_2) . The temperature difference scale changes slowly with frequency ν ; an approximate scale for 1000 cm⁻¹ is drawn in Fig. 2.

The general shape of the extinction coefficient curve for 75 percent H_2SO_4 in Fig. 1 is nearly a mirror image of the Venus spectra in Fig. 2. At maxima in the extinction coefficient the brightness temperature of Venus is a minimum, and vice versa. This is so because there is a temperature gradient at the atmospheric levels observed; at wavelengths where the clouds are more opaque we see a higher, colder level, and where clouds are more transparent we see into a warmer region. Comparison with the extinction curve for 90 percent acid shows poor agreement; in particular, the strong 980 cm^{-1} absorption is absent on Venus. We infer that the concentration of H_2SO_4 in the Venus clouds is much closer to 75 than to 90 percent. Thus, the stratospheric aerosol on Venus is very similar to that on the earth (6).

We can now use the spectral extinction curve for 75 percent H_2SO_4 aerosol and the known temperature gradient (11) of about 4°K/km in the cloudy region to deduce the vertical structure of the clouds from the thermal spectra of Venus. The optical depth $\tau(h)$ above a height h depends on the aerosol density $\rho_n(h)$ and the specific extinction coefficient $\beta(\nu)$; if we assume an exponential aerosol distribution with aerosol scale height h_n , we have

$$\tau(h) = \rho_a(h)\beta(\nu) = \rho_0\beta(\nu) \exp\left[-(h-h_0)/h_a\right]$$

where ρ_0 is the density at a reference height h_0 . Now the temperature profile can be represented by

$$T(h) = T_0 - \Gamma(h - h_0)$$

where $T_0 = T(h_0)$ and $\Gamma \approx 4^\circ \text{K/km}$

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Fig. 2. Thermal emission spectra of Venus, taken from Hanel *et al.* (8) (crosses), Gillett *et al.* (9) (closed circles), and Hanel *et al.* (10) (smooth curve).

We can use this relation to eliminate $(h-h_0)$ from the previous equation, which then becomes

$$\tau(\nu) = \rho_0 \beta(\nu) \exp\left[\frac{T(h) - T_0}{\Gamma h_a}\right]$$

At each frequency ν we see an average brightness temperature $T_{\rm b}$ that is weighted by a function of optical depth. It is a fairly good approximation to say that this average corresponds to the conditions at $\tau = 1$; that is,

$$T_{
m b}(\nu) \approx T[\tau(\nu) \equiv 1]$$

Hence,

$$1 \approx
ho_0 eta(
u) \exp\left[rac{T_{
m b}(
u) - T_0}{\Gamma h_{
m a}}
ight]$$

We can now solve for $T_{\rm b}(\nu)$ to find the thermal emission spectrum:

$$T_{\rm b}(\nu) - T_0 \equiv ({\rm const.}) - \Gamma h_{\rm a} \ln \beta(\nu)$$

I have already remarked that Fig. 2 is essentially such a plot of brightness temperature versus frequency. If we compare two frequencies ν and ν' , we have

$$\Delta T \equiv T(\nu) - T(\nu') \equiv -\Gamma h_{\rm a} \ln[\beta(\nu)/\beta(\nu')]$$

which we can solve for the aerosol scale height h_a :

$$h_{a} = \frac{\Delta T}{\Gamma \ln[\beta(\nu')/\beta(\nu)]}$$

For example, if we compare the Venus spectral peak at 850 cm⁻¹ with the valley at 910 cm⁻¹, we see from Figs. 1 and 2 that $\Delta T \approx 22^{\circ}$ K and $\ln[\beta(850)/\beta(910)] = 1.032$, so that $\Gamma \approx 4^{\circ}$ K/km gives $h_{\rm a} \approx 5.33$ km. This is very nearly the scale height of the gas in the stratosphere of Venus. In other words, the aerosol mixing ratio



Fig. 3. Observed (light line and line with dots) and computed (heavy line) thermal spectra of Venus. The computed model assumes a 75 percent H_2SO_4 aerosol uniformly mixed in a region with a temperature gradient of $4^{\circ}K/km$.

appears to be constant at all levels. Young has pointed out (4) that a constant mixing ratio may be expected, because the terminal velocity of micrometer-sized droplets is some $3 \times$ 10^{-6} of the wind speeds believed to exist in this region. To indicate how well such a cloud model explains the observations, Fig. 3 shows the expected variation of ΔT with frequency, calculated from $\beta(\nu)$ for 75 percent acid aerosol and assuming a well-mixed cloud with a 4°K/km lapse rate, together with the better observational data in this spectral region. The variation in the temperature scale with vhas been neglected. In view of the fact that the model contains several approximations, that Remsberg's $\beta(v)$ values were deduced from room-temperature optical constants, and that the observational temperature scale is somewhat uncertain, the agreement is satisfactory. A comparison of Figs. 1 and 3 suggests that slightly higher acid concentrations might give better agreement.

Obviously, more accurate spectral data on Venus and on H_2SO_4 (especially at temperatures near 250°K and for intermediate concentrations) are urgently needed. Until such data are available, a uniformly mixed aerosol seems a good cloud model.

It is sometimes supposed that such a cloud cannot explain the observed spectroscopic phase effect on Venus, a conclusion based on multiple-scattering models in which either the vertical pressure gradient of the absorbing gas has been ignored or pressure effects have been treated rather crudely. However, the observed square-root curve of growth agrees with saturated, pressurebroadened lines if a modest path-length factor is used to allow for multiplescattering effects (12). It is instructive to lump all scattering effects into the assumption that we always see to the same scattering optical depth (of order unity) in reflected sunlight. Then we should also see a fixed amount of gas: if the sunlight always experiences the same number of scatterings, it must also traverse the same amount of gas in the total path before being scattered back out. The equivalent width of a line W is proportional to the square roots of both the number of absorbing molecules n and the pressure p; that is,

$W \sim (np)^{\frac{1}{2}}$

But I have argued that n, which is the product of the pressure p and the air

mass factor $M \approx \sec Z$, is constant. Hence p = n/M or

$$W \sim M^{-1/2} = (\cos Z)^{1/2}$$

where Z is the angle between the line of sight and the local vertical on Venus. At a phase angle i, we have typically $Z \approx i/2$, so that

$$W \sim [\cos(i/2)]^{\frac{1}{2}}$$

Such a variation is consistent with the observed phase effect for the stronger CO_2 bands (12). For example, the equivalent widths in the 8,689-Å and 10,488-Å CO_2 bands are about $\frac{1}{3}$ as large near 165 deg phase as they are below 60 deg phase. We can also expect that the average gas temperature will vary by only $\pm 3^{\circ}$ K from zero phase to i = 121 deg (assuming a 5-km scale height and 4°K/km lapse rate), but that rotational temperatures observed near 165 deg phase will be some 20°K lower. This also agrees with observation (12, 13).

Finally, a similar argument explains the very weak center-to-limb effect. If we observe at small phase, we expect to find $W \sim (\cos Z)^{\frac{1}{2}}$, so that W is still 0.71 as large at Z = 60 deg (almost nine-tenths of the way from center to limb) as at the center of the disk. Halfway from the center to the limb, Z = 30deg and W is 0.93 as large as at the center of the disk. These small effects are generally not measurable on Venus, because of its small angular size. However, such effects are observed on Jupiter, a similarly cloud-covered planet.

One last piece of evidence supporting a uniformly mixed aerosol may be mentioned. When Venus transits the sun, light is observed refracted through her upper atmosphere. The maximum refraction observed corresponds to pressure levels in the range from 3 to 6 mb (14). This pressure is an order of magnitude lower than the effective pressure of line formation for CO_2 and CO at 60 deg phase, where the effective air mass factor is $M \approx 9$ because of multiple scattering (12). The effective air mass factor for transmitted light at grazing incidence (15) is

$M(90 \text{ deg}) = (2\pi R/h)^{\frac{1}{2}}$

which, for a planetary radius R = 6100km and scale height h = 5 km, is about 88. Thus the increased air mass factor at grazing incidence compensates almost exactly for the lower pressure, and the total amount of gas in the line of sight is practically the same as at 60 deg phase. As both conditions cor-

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respond to an aerosol optical depth near unity, this equality is evidence for a constant aerosol mixing ratio over some 2.3 scale heights. It also supports the phase-invariance of the number of molecules in the line of sight.

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- of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract NAS 7-100, sponsored by the National Aeronautics and Space Administration.
- 27 August 1973; revised 19 October 1973

Suppression of Nitrogen Fixation by Blue-Green Algae in a **Eutrophic Lake with Trace Additions of Copper**

Abstract. Nitrogen fixation by blue-green algae in highly eutrophic Clear Lake, California, was severely inhibited by trace amounts of copper. The chelation capacity of the lake is probably saturated by indigenous copper. Additions were only 1/200 of those normally used in algal control. Since nitrogen fixation provides half of the lake's annual nitrogen budget, economical eutrophication control appears possible.

We report the specific effects of very low concentrations of added and indigenous Cu on phytoplanktonic N₂ fixation and photosynthesis in a lake where natural chelation should be high. In summer, eutrophic Clear Lake, California, contains large quantities of particulate and dissolved organic matter (1, 2). Both these classes of material have been demonstrated to chelate Cu (3).

Copper sulfate has long been used as an algicide in aquatic ecosystems but its use in more subtle ways was unknown hitherto. There have been several reports of inhibition of algal photosynthesis by Cu added at concentrations below those found for soluble Cu in the natural environment (4). These were studies of laboratory cultures of algae grown in the absence of chelating agents. These studies assumed that such low Cu concentrations had no effect in situ because of chelation with various substances. Certainly ethylenediaminetetraacetic acid (EDTA) will rapidly remove the toxic effects of Cu in natural phytoplanktonic populations (5). Thus, if indigenous Cu in a water body is chelated, variations in Cu concentrations should play no role in controlling algae. The effects of small additions of Cu (5 to 10 μ g/liter) should again be small, especially where there is much organic material in the water, because of rapid chelation or precipitation of Cu (5). Our studies have been concentrated on these postulations.

The method used was an extension of the bioassay devised by Goldman (6) which involves simultaneously adding nutrients and NaHCO₃ labeled with ¹⁴C to natural phytoplankton and measuring the changes in ¹⁴C uptake produced, relative to a control. In this case, changes in N2 fixation, chlorophyll a content, species biomass, and composition were also followed. There are three limitations in the use of this bioassay for periods of several days: bottle wall effects, respiration of photosynthetically fixed CO₂, and changes in the ratio O_9/CO_9 resulting from incubation in small impermeable bottles. In experiments in cool oligotrophic lakes these effects do not present serious problems since biomass and rates of activity are low. This is not the case with warm eutrophic lakes such as Clear Lake, where summer chlorophyll a concentrations range from 50 to as much as 80,000 μ g/liter and water temperatures of 25°C are frequent. To overcome such problems we used large flasks