Reports

Venus: Microwave Detection of Carbon Monoxide

Abstract. The 115-gigahertz microwave line of carbon monoxide has been detected in the spectrum of Venus. The measurement proves that the carbon monoxide mixing ratio increases above an altitude of 85 kilometers in the Venus stratosphere and provides quantitative information on carbon monoxide in the altitude region from 80 to 110 kilometers. This altitude region is well above that which has been previously sensed.

The dissociation of CO₂ by solar ultraviolet radiation is a major source of CO in the upper atmospheres of Venus, Earth, and Mars. We here report detection of the $J = 0 \rightarrow 1$ CO rotational transition in the ground vibrational state at a frequency of 115,271.2 Mhz (2.6-mm wavelength) in the spectrum of Venus. This spectral line appears as a narrow absorption feature against the Venus continuum emission. It is the first microwave spectral line to be detected in a planetary atmosphere other than that of Earth, although the use of microwave spectral lines as probes of planetary atmospheres was suggested by Barrett (1) more than 12 years ago. The observed spectral line provides information about CO between the \sim 5.0- and \sim 0.002mbar pressure levels in the Venus stratosphere. The altitude range corresponding to these pressure levels is 80 to 110 km, well above that which has been previously sensed by infrared measurements of CO on Venus

The possible presence of CO in the Venus atmosphere was first reported by



Fig. 1. The 115-Ghz CO absorption in the Venus spectrum measured on 28 August 1975. The measured values are indicated by points. Curves A, B, and C are the calculated profiles for the three different CO mixing ratio curves shown in Fig. 2 and explained in the text. The spectral resolution was 0.25 Mhz, and the average value of the sec Z for the observation was 1.23, where Z is the zenith angle. The relative root-mean-square measurement noise was about 0.01.

Sinton (2), and later verified by Moroz (3), from infrared observations of the first overtone band at $2.35-\mu$ wavelength. The first quantitative measurement was reported by Connes et al. (4) from observations of the same band with a high-resolution interferometer. The measurements of Connes et al. indicated a total effective CO column density of 3.5×10^{20} molecule/ cm² (13 cm amagat). From measurements of nearby CO, bands on Venus, and assuming a constant CO mixing ratio, Connes et al. concluded that the CO/CO, ratio is 4.5×10^{-5} near a pressure level of \sim 175 mbar, which corresponds to an altitude near 65 km.

Our measurement of the $J = 0 \rightarrow 1$ $^{12}C^{16}O$ spectral line on Venus is shown in Fig. 1. The points represent measured values; also shown are spectral features calculated for three different CO profiles as discussed below. As Fig. 1 indicates, the spectral line appears in absorption against the warmer background Venus continuum emission originating at lower altitudes. For temperatures expected in the Venus stratosphere where the spectral line originates the collisional line width parameter is ~ 4 Mhz/mbar, as discussed below, and the observed half width of ~ 0.5 Mhz proves that the absorption originated principally at a pressure of ~ 0.1 mbar. This pressure region is much lower than that to which the infrared measurements mentioned above were sensitive, and corresponds to altitudes above ~ 90 km in the atmosphere of Venus.

Our measurements were made with the antenna (4.6 m in diameter) and millimeter-wave spectral line receiver of the Aerospace Corporation. At 2.6 mm, the antenna half-power beam width is 2.5 arc min, and the observations were made with the use of a position-switched mode. In this mode the antenna position alternated between Venus and an "off" position, 5 arc min east, every 20 seconds. This mode had the advantage of making possible the simultaneous measurement of the continuum and the CO absorption line temperatures-allowing cancellation of all instrumental parameters in computing the percentage absorption. Since the Venus absorption line was observed only in the upper side band of the double side band receiver, and Earth's atmospheric absorption is significantly different in each side band as a result of the O₂ line at 118,750 Mhz, it was necessary to measure and correct for this atmospheric absorption. The average zenith opacity was measured to be 0.38, and, using the atmospheric attenuation data of Ulich and Haas (5), we estimated the values for the upper and lower side band to be 0.56 and 0.28, respectively.

The observations shown in Fig. 1 were made on 28 August 1975, a few hours after inferior conjunction (phase = 0.005) when Venus had an angular diameter of ~ 1 arc min. The velocity shift of the spectral feature due to the relative Venus-Earth motion was +0.3 km/sec for these observations, as expected. A different velocity shift of +1.8 km/sec was observed on 31 August 1975, also as expected. These observed shifts prove that the spectral feature originated on Venus. The terrestrial CO absorption feature, recently measured by Waters et al. (6), has negligible effect on these data because of its smallness and because the observations were made with the position-switched mode.

For the calculated spectral lines shown in Fig. 1, we used the absorption coefficient for this CO transition as given previously (6). The Voigt line shape was used with the standard Doppler line width parameter and with the collisional line width parameter (in megahertz) given by

$$\Delta v = 3.0 p \left(\frac{300}{T}\right)^{0.75}$$
(1)

where p is the total pressure in millibars, and T is the temperature in degrees Kelvin. The numerical coefficient in Eq. 1 was obtained from laboratory measurements of



Fig. 2. The CO mixing ratio profiles used for calculations. Profiles A, B, and C are discussed in the text.

collisional broadening of CO by $CO_2(7)$, since the Venus atmosphere is almost entirely CO₂. The temperature exponent in Eq. 1 is that for quadrupole-quadrupole interactions, which are expected to dominate the collisional broadening of this transition. The 1972 NASA nightside model of the Venus atmosphere (8) was used for the temperature and pressure profiles. We calculated the brightness temperature $T_{\rm B}$ for a normal ray by numerically integrating the radiative transfer equation between altitudes of 60 and 130 km. Above 130 km the contribution to $T_{\rm B}$ is negligible; at 60 km a brightness temperature of 320°K was used for the upwelling radiation, which is based on the measurements of Ulich (9). Since the angular extent of the planet is much less than the antenna beam width, we obtained the disk temperature $T_{\rm D}$ by integrating $T_{\rm B}$ over the planet, assuming spherical symmetry. The fractional absorption of CO was then determined from the relative values of $T_{\rm D}$ at the center of the spectral line and 8 Mhz away, respectively. We estimate that the errors due to the numerical calculation process are less than 1 percent.

Three of the CO mixing ratio profiles used in the calculation are shown in Fig. 2. The corresponding calculated spectra are given in Fig. 1 with the measured spectrum. Because of pressure broadening of the CO line, our measurement is relatively insensitive to CO below ~ 80 km. In the range from 85 to 100 km the measurement is very sensitive to the CO mixing ratio profile. Above ~ 105 km the measurement is sensitive only to the total column density of CO, because of the dominance of the Doppler broadening which is a weak function of altitude.

Profile A of Fig. 1 is that calculated by Liu and Donahue (10) for an eddy diffusion coefficient of 10⁶ cm² sec⁻¹, and gives the best fit to our measurement of the profiles reported by Liu and Donahue and by Sze and McElroy (11). However, profile A implies an absorption feature that is significantly narrower and slightly stronger than given by the measurements, an indication that it gives too much CO at higher altitudes and too little at lower altitudes. A preliminary comparison of our measurements with the CO distribution recently calculated by Dickinson and Ridley (12) indicates that their calculated distribution has more nightside CO than implied by our measurement. Further measurements of the spectral line reported here will determine the extent of diurnal variation of CO in the upper atmosphere of Venus.

Profile B illustrates a CO mixing ratio profile that is consistent both with our measurement and with the infrared measurement of Connes et al. (4), which is sen-

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sitive to CO at lower altitudes. Profile C differs from profile B only in having more CO in the altitude region from 87 to 102 km and illustrates the sensitivity of our measurement to this altitude region. Because our measurement provides quantitative information on CO at higher altitudes on Venus than has been previously available, it should lead to the development of more precise photochemical models of the upper atmosphere of Venus.

Note added in proof: On 9 November 1975 we detected the 115-Ghz microwave line of CO in the spectrum of Mars also. The 11-m-diameter antenna of the National Radio Astronomy Observatory located on Kitt Peak, Arizona, was used for this observation

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Protein Purification: Adsorption Chromatography on Controlled Pore Glass with the Use of Chaotropic Buffers

Abstract. Chromatography on controlled pore glass in combination with chaotropic buffers makes possible, in a single step, protein purifications of several hundredfold. The new emphasis is on highly selective controllable adsorption. The method is useful for the purification and concentration of proteins from large volumes of complex media and for the purification of proteins that are poorly soluble or tend to aggregate in aqueous solution. $D-(-)-\beta-Hydroxybutyrate$ dehydrogenase, a mitochondrial membrane-bound protein, several soluble proteins, and staphylococcal α toxin, which can be purified directly from large volumes of culture medium, are used to illustrate the method.

Controlled pore glass (CPG), first introduced by Haller, has been used for the separation of a number of biologically interesting compounds (1). In most of these applications, the separation is based mainly on differences in molecular size. We now describe a new procedure for the purification of proteins which emphasizes the use of adsorption chromatography on CPG in combination with chaotropic buffers. The high adsorption affinity of CPG allows rapid concentration and buffer replacement for proteins from large volumes of salts, sugars, or culture media. Selectivity in the elution of proteins is achieved by the use of different chaotropic eluting agents, by varying the pH, and by changing the ionic strength. Purifications of several hundredfold have been achieved with this method. The technique is illustrated in the purification of several types of proteins, including a membrane protein, several soluble proteins, and an exotoxin.

The column packing chosen was CPG-

10-350 (75- to 125- µm particles; Electro-Nucleonics). The particular lots used had mean pore diameters of 313 to 368 Å with surface areas of between 62 and 75 m^2/g . The pore size selected precludes the entry of membranous material into the inner volume of the CPG, effectively limiting the adsorption process to soluble proteins or small aggregates. Used CPG can be reclaimed either by washing in a mixture of persulfate and sulfuric acid for several days or by heating on a steam bath with 10 percent nitric acid for several hours, followed in either case by repeated washing with water to neutrality. However, the beads are sensitive to strong alkali, as well as to hydrofluoric acid, and both should be avoided.

The application of the CPG method to the purification of the apoenzyme form of $D-(-)-\beta$ -hydroxybutyrate dehydrogenase (BDH) (E.C. 1.1.1.30) is of interest since BDH is a mitochondrial membrane-bound protein that has a tendency to aggregate in