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TITAN: DISCOVERY OF CARBON MONOXIDE IN ITS ATMOSPHERE

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Abstract. We have identified the 3-0 rotation-vibration band of carbon monoxide in the near-infrared spectrum of Titan and have determined a preliminary mixing ratio $\text{CO}/\text{N}_2 = 6 \times 10^{-5}$. This result supports the probable detection of CO_2 by Samuelson et al. (7) and strengthens possible analogies between the atmosphere of Titan and conditions on the primitive Earth.

Saturn's satellite Titan has been known to have an atmosphere since methane was discovered in its spectrum in 1944 (1). However, the large mass and marvelous complexity of its nitrogen-dominated atmosphere was not realized until the successful Voyager I flyby in 1980 (2,3). The list of atmospheric constituents has grown steadily with subsequent analyses of the Voyager data.

These spectroscopic identifications, when combined with the mean molecular weight deduced for the atmosphere, seem to indicate that argon may be among those constituents which are present in large quantities (4). This possibility further suggests a model for Titan in which the entire atmosphere is formed as a result of degassing of hydrates frozen as clathrates in the mantle during formation (5). In this model, much of the N_2 we now see in the atmosphere could have been trapped in this way, provided that the proto-Saturnian nebula contained nitrogen in this diatomic form, rather than in ammonia. This assumption carries with it the prediction that some CO would be trapped as well. This association of CO with N_2 in the nebula (6) provided the original

motivation for a search for CO on Titan. The subsequent discovery of CO₂ in Titan's atmosphere (7) gave additional impetus to this search, since the existence of CO₂ in such a reducing environment strongly implies the presence of CO as a precursor.

Here we report the successful result of our search and derive a preliminary estimate of the CO/N₂ mixing ratio.

During the week of 1-5 June 1982, we recorded a series of spectra of Titan in the 1.6 μm atmospheric window at a resolution of 1.2 cm^{-1} with the coude Fourier Transform Spectrometer and the 4-meter Mayall telescope at Kitt Peak National Observatory. The signal-to-noise ratio of the co-added spectra (from 5600 to 7200 cm^{-1}) is approximately 40:1, reached with a total integration time of 7.5 hours. Figure 1 shows a portion of this spectrum in the region from 6300 to 6380 cm^{-1} , along with spectra of Uranus recorded under similar conditions during the same observing run. A comparison of these two shows that the spectrum of Titan contains strong absorptions not present in the spectrum of Uranus. These additional Titanian absorptions are readily identified as the P- and R-branches of the 3-0 rotation-vibration band of CO. The predicted line positions are also indicated in Figure 1; and indeed, two of the lines, P(3) and P(4), occur in a region uncontaminated by either solar lines or methane absorptions.

Since the atmosphere of Uranus contains no appreciable CO and its spectrum is dominated by methane in the 1.6 μm window (with

the exception of CH_3D absorption near 6425 cm^{-1} (8)), we used our observations of Uranus to estimate the contribution of methane absorption to the Titan spectrum. Although the atmospheric structures of the two objects are very different, there is a striking similarity between the overall shapes of the methane absorptions, with those of Uranus being somewhat deeper. Consequently, after correcting for the relative Doppler shifts and scaling the absorption depths, we used Uranus as a reference to eliminate the major effects of the methane absorption as well as the solar and telluric lines in the Titanian spectrum. The resulting residual spectrum, shown in Figure 1 for illustrative purposes only, is at best a first-order approximation to the low-temperature behavior of methane in this spectral region, but we consider it sufficient for the preliminary analysis reported here.

Although CO is unequivocally present in Titan's atmosphere and we can trace its contribution to the spectrum by P- and R-branch lines up to $J = 9$, it is not a simple matter to determine its mixing ratio from these observations because of the presence of aerosols and possibly clouds. However, for this preliminary report we have used a simple reflecting layer model (RLM) to establish the order of magnitude of the CO abundance.

For the RLM we assumed that at these wavelengths we are "seeing" to the satellite's surface or to a dense cloud layer just above it. This hypothesis is the basic premise of the RLM and in this case gains

credence from the observation that weak methane bands in this spectral region correspond to a column abundance that is some ten times larger than abundances derived from bands with comparable strengths at visible wavelengths (9,10).

We computed synthetic spectra for all P(J) and R(J) lines with $J < 10$, shown in Figure 1, and derived a best fit to the residual spectrum with a total line-of-sight column abundance of $n_a = 15$ m-amagats, where $n = 3$ for the geometry of our observations. Using a surface pressure of 1.6 bars as determined by the Voyager radio occultation team (2) and assuming that N_2 constitutes 82% of the bulk atmosphere as proposed by the Voyager IRIS team (3), we derived a mixing ratio of $CO/N_2 = 6 \times 10^{-5}$.

This RLM is in fact a gross simplification of the radiative transfer in the atmosphere of Titan. First, our RLM estimate of the CO/N_2 mixing ratio could be significantly less than the actual amount if the "reflecting layer" lies much higher than the radio occultation surface at 1.6 bars. In view of the large column density estimated for CH_4 in this spectral region, this circumstance seems unlikely, but nevertheless is a potential source of uncertainty in the RLM.

Secondly, the RLM ignores the enhancing effects of scattering on absorption by weak lines such as these, the result of which is to overestimate the abundance and to fail to account for observed line shapes. This latter inability of the RLM is evident in Figure 1

where the sharpness of the CO lines in the synthetic spectrum fails to match the observed shapes in the residual spectrum.

We encountered this same type of mismatch in our RLM analysis of CH₄D in the spectrum of Titan near 6425 cm⁻¹ and found that the introduction of a scattering haze is required to account for the observed line shapes of CH₄ (8). In the 6425 cm⁻¹ region, where we have been able to estimate the temperature dependence of CH₄ absorption (8), a model with a thin haze layer overlying clear gas above a thick cloud provides rather satisfactory agreement with the observed spectrum. This two-cloud model (TCM) yields a CH₄ column density of $\eta_a = 2.2 \text{ km} \cdot \text{amagats}$, which again suggests that we are in fact seeing very deep. If the dense cloud corresponds to the radio occultation surface at 1.6 bar, the model further yields a CH₄/N₂ mixing ratio near 10⁻², in agreement with the Voyager estimates.

Consequently, we have used the same model for the CO analysis. The preliminary results are encouraging: although not yet entirely satisfactory, this TCM provides an improved fit to the observed band structure over that for the RLM. We obtain from this model a preliminary CO column abundance of $\eta_a = 12 \text{ m} \cdot \text{amagats}$ above the dense cloud and a CO/N₂ mixing ratio of 5×10^{-5} if the dense cloud is at 1.6 bar.

A considerable amount of additional work has yet to be done to establish our final estimate of the amount of CO in Titan's atmosphere. Proper account of the temperature dependence of methane

absorption in the 6300 cm^{-1} region is required to obtain an improved residual spectrum. Similarly, a refined atmospheric model appropriate to this region is needed to improve the fit of the synthetic line profiles with the observations; and perhaps better observations above our present signal-to-noise level of 40 may be necessary. We are continuing our research efforts along these lines; but in the meanwhile, we believe that we have established the abundance of CO in Titan's atmosphere to within a factor of two.

The detection of CO in this amount requires some additional discussion in light of the large CO abundance predicted by the photochemical model used to explain the CO₂ detection (7). If the influx of H₂O (assumed to be the source of the OH radical required in the key reactions producing CO₂) into the satellite's atmosphere is about one-tenth the value associated with the meteoritic infall on the Earth, the observed CO₂ abundance implies $\text{CO}/\text{N}_2 = 1.4 \times 10^{-3}$ (7). Our result is well below this prediction, requiring a very large influx of H₂O if the proposed reaction scheme is correct, greater than that on Earth. Thus, our abundance determination implies either that a large local source of icy grains exists in the vicinity of Titan (e.g., the E ring, impact debris from outer satellites) or other reaction pathways to convert CO to CO₂ must be found. In either case, the discovery of CO supports the probable identification of CO₂ reported by Samuelson et al. (7), but it does not necessarily follow that the CO we see now was captured from the nebula as a clathrate by the forming satellite

and is not the result of photochemical reactions. An unambiguous detection of ^{36}Ar remains the best evidence for clathrate capture process.

The addition of some 50 ppm of CO to Titan's atmosphere, with the concomitant implication of active OH, makes this atmosphere even more interesting as a natural laboratory for testing our ideas about chemistry on the pre-biological Earth. Recent thinking has suggested that the early Earth may have had an atmosphere that was less reducing than the traditional Miller-Urey model (11). Titan departs most drastically from this revised Earth model in being far too cold to permit the existence of liquid water. Nevertheless, atmospheric chemical reactions taking place on Titan today may resemble some of those that occurred on the early Earth. Of particular interest is the issue of preferential pathways: are some routes towards chemical synthesis favored over others? The 93 K surface will serve as a cold trap for any complex organic aerosols that precipitate from the atmosphere; and with the presence of both HCN and CO established, these compounds should include many of biological interest (12).

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FIGURE CAPTION

Figure 1. Spectra of Uranus (a) and Titan (b) in the 6350 cm^{-1} region at a resolution of 1.2 cm^{-1} , obtained with the Fourier Transform Spectrometer and the 4-meter telescope at Kitt Peak National Observatory. Residual Titan spectra (c) obtained after using the Uranus spectrum to correct for the major effects of methane, telluric, and solar absorption (see text for details). Synthetic spectrum of CO (d) computed for a reflecting layer model of Titan. At top are the rotational assignments and position for the CO 3-0 rotation-vibration band.

