Reports

Titan: Discovery of Carbon Monoxide in Its Atmosphere

Abstract. *The 3-0 rotation-vibration band of carbon monoxide in the near-infrared spectrum of Titan has been identified, and a reflecting layer model mixing ratio of carbon monoxide to molecular nitrogen of* 6×10^{-5} *has been determined. This result supports the probable detection of carbon dioxide by Samuelson and his co-workers and strengthens possible analogies between the atmosphere of Titan and conditions on primitive Earth.*

Saturn's satellite Titan has been known to have an atmosphere since CH_4 was discovered in its spectrum in 1944 (*1*). However, the large mass and marvelous complexity of its N_2-dominated atmosphere were 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, allow the presence of a large amount of argon (*2, 4*); the presence of argon suggests a model in which the entire atmosphere is a result of degassing by clathrates frozen in the mantle during formation (*5*). If most of the N_2 we now see in the atmosphere was indeed trapped from the proto-Saturnian nebula in this way, it would imply that some CO would be present as well (*6*). This association of CO with N_2 in the nebula (*6*) provided us with the original motivation for a search for CO on Titan. The subsequent discovery of CO_2 in Titan's atmosphere (*7*) gave additional impetus to this search, since the presence of CO_2 in such a reducing environment strongly implies the presence of CO as a precursor.

During the week of 1 to 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 coudé Fourier transform spectrometer and the 4-m 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 1b shows a portion of this spectrum in the region from 6300 to 6380 cm^{-1}, along with a spectrum of Uranus recorded under similar conditions during the same observing period (Fig. 1a). A comparison shows that the spectrum of Titan contains strong absorptions not present in the spectrum of Uranus. These additional 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 Fig. 1; two of the lines, *P*(3) and *P*(4), occur in a region uncontaminated by either solar lines or CH_4 absorptions.

Since the atmosphere of Uranus contains no appreciable CO and its spectrum is dominated by CH_4 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 CH_4 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 CH_4 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 CH_4 absorption as well as the solar and telluric lines in Titan's spectrum. The resulting residual spectrum, shown in Fig. 1c for illustrative purposes only, is at best corrected for a first-order approximation to the low-temperature behavior of CH_4 in this spectral region, but we consider it sufficient for the analysis reported here.

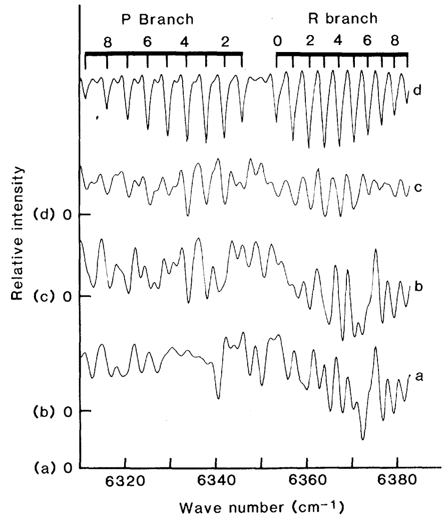

Fig. 1. Spectra of Uranus (a) and Titan (b) in the 6350-cm^{-1} region at a resolution of 1.2 cm^{-1}, obtained with the Fourier transform spectrometer and the 4-m telescope at Kitt Peak National Observatory. Residual Titan spectrum (c) obtained after the Uranus spectrum was used to correct for the major effects of CH_4, telluric, and solar absorption (see text). Synthetic spectrum of CO (d) computed for a reflecting layer model of Titan. At the top are the rotational assignments and position for the CO 3-0 rotation-vibration band.

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* (rotational quantum number) = 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 report we have used a simple reflecting layer model (RLM) to establish the order of magnitude of the CO abundance.

For the RLM we assume that at these wavelengths we are "seeing" to the satellite's surface or to a dense cloud layer just above it. Support for this assumption comes from the observation that weak CH_4 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*).

We computed synthetic spectra for all $P(J)$ and $R(J)$ lines with $J < 10$ (Fig. 1d) and derived a best fit to the residual spectrum with a total line-of-sight column abundance of $\eta a = 15$ m-amagats, where the air mass factor (η) is equal to 3 for the geometry of our observations. Using a surface pressure of 1.5 bars as determined by the Voyager radio occultation team (*2*) and assuming that N_2 constitutes 82 percent of the bulk atmosphere as proposed by the Voyager IRIS (infrared instrument) team (*4*), we derived a mixing ratio of CO to N_2 of 6×10^{-5}.

The RLM fails to match the observed shapes in the residual spectrum (Fig. 1c). We encountered this same type of mismatch in our RLM analysis of CH_3D near 6425 cm^{-1}, where we have been able to estimate the temperature dependence of CH_4, and found that the introduction of a scattering haze layer overlying the clear gas is required to account for the observed line shapes (*8*). This two-cloud model (TCM) yields a CH_4 column density of the order of $a = 2.2$ km-amagats, which once again suggests that we are "seeing" very deep into the atmosphere. If the dense cloud corresponds to the radio occultation surface at

1.5 bars, the model yields a CH_4/N_2 mixing ratio near 0.03.

We have used the TCM for a preliminary CO analysis; the results are encouraging, although not yet entirely satisfactory. This TCM provides an improved fit to the observed band structure over that for the RLM and yields a preliminary CO column abundance of $a = 12$ m-amagats above the dense cloud and a CO/N_2 mixing ratio of 1.5×10^{-4} if the dense cloud is at 1.5 bars.

A considerable amount of work, including taking proper account of the temperature dependence of CH_4 absorption in the 6300-cm^{-1} region, remains to be done before we can precisely estimate the amount of CO in Titan's atmosphere. A refined atmospheric model appropriate to this region is needed to improve the fit of the synthetic line profiles to the observations, and perhaps better observations above our present signal-to-noise level of 40 may be necessary. We believe that we have established the abundance of CO in Titan's atmosphere to within a factor of 3.

The steady-state CO abundance predicted by the photochemical model used to explain the CO_2 detection is $CO/N_2 \gtrsim 1.1 \times 10^{-4}$ (*7*). Our result appears consistent with this prediction. The steady-state CO abundance is independent of the influx of H_2O (assumed to be the source of the OH radical required in the key reactions producing CO_2), if that influx is greater than about 0.3 of the value associated with meteoritic infall on Earth (*7*). Our abundance determination may support the photochemical model suggested; but, in any event, it confirms the proposed identification of CO_2 (*7*). It now seems unlikely that it can provide any information on the primordial CO abundances or direct support of the clathrate model. An unambiguous detection of ^{36}Ar remains the best evidence for the clathrate capture process.

The addition of 50 to 150 parts per million 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 ideas about chemistry on prebiological Earth. Recent thinking has suggested that early Earth may have had an atmosphere that was less reducing than the traditional Miller-Urey model (*10*). Titan departs most drastically from this revised Earth model in being far too cold to permit the presence of liquid water. Nevertheless, atmospheric chemical reactions taking place on Titan today may resemble some of those that occurred on early Earth. Of particular interest is the issue of preferential pathways: Are some routes toward chemical synthesis favored over others? The Titan surface (95 K) serves 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 (*11*).

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Reversible Loss of Gravitropic Sensitivity in Maize Roots After Tip Application of Calcium Chelators

Abstract. *The application of calcium chelating agents (EDTA or EGTA) to the tips of maize roots caused a loss of gravitropic sensitivity. When the chelator was replaced with calcium chloride, gravitropic sensitivity was restored. Asymmetric application of calcium chloride near the tip of a vertical root caused curvature toward the calcium source. When the calcium was applied to the upper surface of the tip of a root oriented horizontally, the root curved upward even though control roots exhibited strong downward curvature. Application of calcium chloride to the tips of decapped roots, which are known to be gravitropically insensitive, did not restore gravitropic sensitivity. However, asymmetric application of calcium chloride near the tips of decapped roots caused curvature toward the calcium source. Calcium may play a key role in linking gravity detection to gravitropic curvature in roots.*

Within 10 to 15 minutes after maize seedlings are oriented horizontally, the primary roots begin to exhibit positive gravitropism. The gravity-detection mechanism is located within the root cap even though the asymmetric growth which causes curvature occurs in the elongation zone behind the root cap (*1*, *2*). Although there is evidence that gravity detection in root cap cells involves the dense amyloplasts (*2*), there is little information on the link between gravity detection and the induction of asymmetric growth in the elongation zone. Recently, calcium has been implicated in gravitropic responses in plants. Calcium moves toward the upper side of gravistimulated hypocotyls and coleoptiles (*3*), and the amyloplasts in the root cap carry substantial amounts of calcium (*4*). Calcium is required for the transport of auxin, a hormone that may mediate asymmetric growth in gravitropism (*5*).

We have examined the effect of calcium depletion and replenishment on gravitropic sensitivity in maize roots. We find that calcium chelators (EDTA or EGTA) applied to the root cap cause loss of gravitropic sensitivity and that sensitivity can be restored if the chelator is replaced with $CaCl_2$. The experiments were done on 3-day-old maize seedlings, and the test chemicals were applied in agar blocks placed directly on the root (*6*).

When 50 m*M* EDTA (*7*) was applied to the tip of the root and the root was immediately oriented horizontally and maintained in that orientation for 180 minutes, no gravitropic curvature oc-