Titan's Thermal Emission Spectrum: Reanalysis of the Voyager Infrared Measurements

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We have modeled the far-infrared spectrum of Titan between 200 and 600 cm⁻¹, including the fine structure of the H₂–N₂ and H₂–CH₄ dimers around 355 and 585 cm⁻¹ respectively. A selection of 373 Voyager IRIS spectra recorded at low and mid-latitudes provides the observational basis for our analysis. The opacity model is significantly improved over previous work by taking into account recent ab initio calculations of the collision-induced absorption by N₂–CH₄ pairs, as well as laboratory measurements of the H₂–N₂ dimer transitions. In addition to the collision-induced gaseous absorption, the radiative transfer model includes scattering and absorption by stratospheric haze particles and potential tropospheric condensation clouds. We investigate the possible presence of argon, mainly through its influence on the thermal profile retrieved from the Voyager radio occultation measurements. We find the following results: (1) The observations are best fit with significant methane supersaturation in the troposphere (up to a factor of two) and no condensation cloud present. (2) If a condensation cloud is present we find that it must have an optical depth less than 0.7 with a mean particle radius of about 50 μm and be located very near the minimum temperature level around 40 km, significantly higher than the expected condensation level. (3) In any case, the CH₄ mole fraction at the cold trap is 0.017–0.045, the H₂ mole fraction is 1.0 ± 0.4 × 10⁻³, the argon mole fraction is less than 0.06 (3σ), and the imaginary index of refraction of the haze material at 600 cm⁻¹ is 30–80% that of tholins. © 1995 Academic Press, Inc.

1. INTRODUCTION

The far-infrared spectra of Titan measured by the IRIS spectrometer on the Voyager spacecraft have revealed crucial information on the physical and chemical properties of the atmosphere of Saturn's largest moon. The analysis of these data, combined with that of the radio occultation measurements resulted in the first determination of the thermal profile and atmospheric structure (Samuelson et al. 1981, Lellouch et al. 1989, Toon et al. 1988). Knowledge of the upper atmospheric composition has also progressed considerably thanks to these data (Coustenis 1990, Gautier 1985, 1992a), as well as information on the stratospheric haze (Samuelson and Mayo 1991) and on atmospheric dynamics (Flasar et al. 1981, Flasar and Conrath 1992).

One of the unresolved issues concerns the possible presence of an undetected major atmospheric constituent other than N₂, CH₄, and H₂, which have been spectroscopically identified. This question stems from the fact that the mean molecular mass may be substantially higher than 28 (Samuelson et al. 1981), which would require the presence of an element heavier than nitrogen. Argon is the most likely candidate since it is cosmically abundant and would not condense under Titan's atmospheric conditions (Owen 1982). The present error bar on the mean molecular mass, resulting from the work of Lellouch et al. (1989), allows values of the argon mole fraction between 0 and 21%, while the upper limit on the EUV argon emission around 1048 and 1065 Å, derived from the UVS experiment, sets an upper limit of 14% at the tropopause (Strobel et al. 1992). Recently, Strobel et al. (1993) refined their analysis and lowered that upper limit to 10%.

The present study consists of a reanalysis of Voyager IRIS spectra in the 200- to 600-cm⁻¹ range, with emphasis on the interpretation of the "dimer features" observed around 355 and 585 cm⁻¹, in the S(0) and S(1) rotational transitions of molecular hydrogen. Similar features, although corresponding to different conditions, have already been observed by the same experiment on Jupiter and Saturn (Gautier et al. 1983, McKellar 1984). On these
planets, the molecular species involved are the $\text{H}_2\text{-H}_2$, Van der Waals complexes, whereas on Titan they are the $\text{H}_2\text{-N}_2$, $\text{H}_2\text{-CH}_4$, and possibly $\text{H}_2\text{-Ar}$ associations, if argon is indeed present. The first identification of the $\text{H}_2\text{-N}_2$ features in the IRIS spectra of Titan was proposed by Fox and Kim (1984a,b). It was later confirmed by the analysis of Borysow and Fromhold (1986a). A preliminary quantitative study by Courtin et al. (1988) gave an estimate of the $\text{H}_2$ mole fraction of $1.8 \pm 0.6 \times 10^{-3}$.

By studying these features in more detail, we hope to obtain a more accurate determination of the hydrogen mole fraction and to narrow down the range of possible values for other model parameters, in particular the cloud optical thickness and the argon abundance. In this way, it is complementary to the previous analyses based on the far-infrared thermal emission spectrum, namely those of Samuelson et al. (1981), Toon et al. (1988), and Lellouch et al. (1989). One outstanding problem in the analysis of Samuelson et al. and Toon et al. was matching the IRIS data in the 200- to 400- cm$^{-1}$ interval without invoking an additional source of opacity. Samuelson et al. suggested a methane condensation cloud adding such a contribution in the troposphere, while Toon et al. arbitrarily increased the gaseous $\text{N}_2\text{-CH}_4$ absorption by a factor of 2 (consistent with the uncertainty about that absorption at the time). As far as argon is concerned, whereas Toon et al. interpreted the thermal emission under the assumption that no argon was present, Lellouch et al. did explore the influence of argon on the thermal structure, and thus on the infrared spectrum, but limited their study to the $\nu_4$ band of $\text{CH}_4$ around 1304 cm$^{-1}$. Now that the collision-induced absorption of $\text{CH}_4$ is much improved, it becomes possible to ascertain the plausibility of these earlier interpretations.

This article is organized as follows: Section 2 briefly describes our selection of IRIS spectra. The atmospheric structure and radiative transfer method are presented in Section 3, along with the gas and particulate opacities. Section 4 details the various cases that we computed and their comparison with the data. The results are summarized and discussed in Section 5.

2. VOYAGER IRIS DATA SELECTION

The data from the Voyager IRIS experiment that we selected for this study correspond to an average of $n = 373$ spectra recorded within $2 \times 10^6$ km from Titan and at latitudes within $\pm 60^\circ$. Secant values range from 1.0 to 2.0, with a mean of 1.23 ($\mu = \cos \theta = 0.81$). The spectral resolution is 4.3 cm$^{-1}$. Figure 1 displays the average brightness temperature spectrum $T_B(\sigma)$ as a function of wavenumber $\sigma$ between 180 and 640 cm$^{-1}$. In Fig. 2, we have plotted the IRIS observations within both the $S(0)$ and the $S(1)$ rotational transitions of $\text{H}_2$, in differential units. The wavenumber origins are $\sigma_S = 354.4$ cm$^{-1}$ and $\sigma_{S_1} = 587.0$ cm$^{-1}$, and the brightness temperature origins are 80.0 and 91.3 K, respectively. The $3 \times \text{NET}_B$ (noise equivalent brightness temperature) error bars were calculated from the instrumental NESR($\sigma$) (noise equivalent spectral radiance) measured for deep space, using the relation

$$\text{NET}_B(\sigma) = \text{NESR}(\sigma) \sqrt{n} \left( \frac{\partial B_\sigma}{\partial T_B} \right),$$

where $B_\sigma$ is the Planck function.

![Figure 1](image1.png)  
**FIG. 1.** The far-infrared spectrum of Titan measured by the Voyager 1 IRIS investigation. The data represent an average of 373 individual spectra recorded within a distance of $2 \times 10^6$ km, within $\pm 60^\circ$ latitude, and airmass less than 2.0. The spectral resolution is 4.3 cm$^{-1}$. The rectangles are centered on the $S(0)$ and $S(1)$ rotational transitions of $\text{H}_2$ (see Fig. 2).

![Figure 2](image2.png)  
**FIG. 2.** A differential plot of the IRIS measurements shown in Fig. 1 within the $S(0)$ and $S(1)$ lines of $\text{H}_2$. The wavenumber origins are 354.4 cm$^{-1}$ for the $S(0)$ and 587 cm$^{-1}$ for the $S(1)$, whereas the brightness temperature origins are respectively 80.0 and 91.3 K. The error bars correspond to $3 \times \text{NET}_B$, derived from the instrumental noise measured for deep space.
The large number of spectra in our sample is needed to warrant a sufficiently high signal-to-noise ratio for the faint dimer features that we wish to study. Inevitably, one expects a significant degree of inhomogeneity in the sample, mainly because of the variations in viewing angle and also because of possible regional differences in the thermal structure, haze properties, or cloud cover. As a matter of fact, the standard deviation of $T_B$ in our sample is typically 10–40 times larger than the instrumental noise shown in Fig. 2. However, we believe that these inhomogeneities do not distort the shape of the spectrum, nor the structure of the hydrogen dimer transitions.

Several molecular bands appear in emission in Fig. 1, at 220, 233, 328, 628, and 633 cm$^{-1}$. They correspond to stratospheric emission from C$_2$H$_2$, C$_2$N$_2$, C$_3$H$_4$, C$_4$H$_2$, and C$_4$H$_4$, respectively. To simplify the radiative transfer computations, we have not included the bands in our model, even though the contributions from the latter three, either on the red side of the $S(0)$ or on the blue side of the $S(1)$ lines, are not completely negligible. Their influence will be discussed in more detail in Section 4.2.

On the basis of the comparison shown in Fig. 2, we also remark that the IRIS data in the two regions do not exhibit exactly the same fine structure, contrary to what is observed in the laboratory for the two hydrogen transitions (see Section 3.2). The obvious differences are the presence in the $S(1)$ line of a pronounced hump at $\delta \sigma = -11$ cm$^{-1}$ ($\sigma = 576$ cm$^{-1}$) and that of a less prominent one at $\delta \sigma = +8$ cm$^{-1}$ ($\sigma = 595$ cm$^{-1}$). It is quite likely that these features are not associated with the hydrogen dimer transitions, but represent instead emission from other molecular species. We will discuss that possibility in the following sections. Additionally, the instrumental noise is clearly much higher in the $S(1)$ line than in the $S(0)$ line. These two caveats lead us to put more confidence in the inference of model parameters from the $S(0)$ line than from the $S(1)$ line.

3. MODEL DESCRIPTION

3.1 Atmospheric Structure

Our baseline atmospheric model is the one developed by McKay et al. (1989). It is divided into 30 homogeneous plane-parallel layers and extend from the surface to 300 km altitude. The corresponding pressure limits in the case where argon is omitted are 0.06 and 1440 mbar (with 10% of argon, the surface pressure reaches a value of 1460 mbar). The model contains four molecular constituents (N$_2$, CH$_4$, H$_2$, and Ar), a tropospheric methane cloud, and a stratospheric haze.

The hydrogen and argon mole fractions are specified as $f_{H_2}$ and $f_{H_2}$. The methane mole fraction $f_{CH_4}$ varies with altitude in the following manner: At the surface, it is scaled from the saturated value by specifying the relative humidity $H_{CH_4}$. It is then held constant up to the altitude where the partial pressure of methane equals its saturated value, around 5 km. It then follows the saturated profile up to the cold trap around 30 km, above which it stays constant. The cold trap is defined here as the level at which the mole fraction reaches its minimum value. It is significantly lower than the level of minimum temperature which is located around 40 km. In certain models, we have allowed the methane distribution to become supersaturated in the upper part of the troposphere. In that case, the CH$_4$ mole fraction is constant between the surface and the level where it reaches a value equal to $S_{CH_4}$ times the saturated mole fraction (for instance, around 15 km for a value $S_{CH_4} = 2.0$). It then follows a profile which is parallel to the saturated one up to the cold trap, which again determines the stratospheric mole fraction. Supersaturation thus occurs between 5 and 40 km, and the supersaturation factor varies with altitude in order to maintain a continuous methane distribution. The stratospheric methane mole fraction is determined only under the assumption that methane is well-mixed above the tropopause, neglecting any photochemical sink. This is because the information contained in the IRIS spectra below 600 cm$^{-1}$ is not sufficient to constrain the methane distribution in the stratosphere. Finally, models with a constant CH$_4$ distribution were also tested. The various methane distributions are summarized in Fig. 3.

In the case labeled "distributed cloud," a condensation cloud is included for all layers where the methane
mixing ratio reaches its saturated value (from ~5 to 30 km altitude). The cloud particles all have the same size, with a radius of $r_{\text{cloud}}$. The opacity is distributed proportionally to the gaseous methane concentration within each saturated layer. The integrated cloud optical depth $\tau_{\text{cloud}}$ is specified at a wavenumber of 200 cm$^{-1}$. We have also constructed a "cold cloud" case in which a condensation cloud is located near the level of minimum temperature ($z \sim 40$ km), independently of the methane distribution.

The stratospheric haze is implemented through a simple microphysical model, of which we have fixed some of the parameters, following the results of McKay et al. (1989): the mass production rate ($1.2 \times 10^{-14}$ g cm$^{-2}$ sec$^{-1}$), the pressure level of peak production ($10^{-4}$ mb), and the characteristic radius (0.09 µm) above which electrostatic charging becomes the limiting factor for the growth of particles. All particles are assumed to have the same size in a given atmospheric layer. Because the haze particles are Rayleigh absorbers—much smaller than the thermal infrared wavelength—theyir opacity depends only on the absorption times the total volume of particles. It is insensitive to the details of the particle size distribution. Since our particle volume is determined by the microphysical model, we adjust the absorption to obtain the opacity needed to match the data.

The thermal profile is determined from the results of the Voyager 1 ingress radio occultation measurements published by Lindal et al. (1983). The same iterative procedure described in McKay et al. (1989) has been applied to calculate the temperature profiles corresponding to various compositional assumptions: The Lindal et al. profile is used to generate an initial methane distribution, the hydrogen and argon mole fractions being held constant with altitude. This fully determines the molecular mass and hence the density profile from which a new temperature structure is derived by scaling the radio occultation data. This process is repeated until sufficient convergence has been reached (i.e., when the temperature increment at the surface becomes less than 0.001 K). Our assumption for the methane—nitrogen equation of state (the nonideal Benedict–Webb–Rubin relation) differs from that used by Lellouch et al.(1989); however, for similar compositions, the differences in surface temperature between their models and ours are at most 0.7 K, the Lellouch et al. profiles being systematically warmer.

In the bottom layers of our atmospheric model, below 7 km altitude, a correction to the local temperature is made during the iterative process whenever the thermal gradient exceeds the dry adiabatic lapse rate. These adjustments are only significant for vacuums of the argon mole fraction above 5%. Although this procedure is inelegant compared with that proposed by Flasar (1983), its impact on the calculated radiance is negligible.

\[ \begin{align*}
    \text{H}_2 & \quad \text{N}_2 & \quad \text{CH}_4 & \quad \text{Ar} \\
    \text{H}_2-\text{H}_2 & \quad \text{N}_2-\text{N}_2 & \quad \text{CH}_4-\text{CH}_4 & \quad \text{Ar-}\text{Ar} \\
    \text{H}_2-\text{N}_2 & \quad \text{N}_2-\text{CH}_4 & \quad \text{CH}_4-\text{Ar} & \quad \text{N}_2-\text{Ar} \\
    \text{H}_2-\text{CH}_4 & \quad \text{N}_2-\text{Ar} & & \\
    & & & \end{align*} \]

**FIG. 4.** Schematic diagram showing all the interacting pairs of Titan’s atmospheric constituents that can produce significant collisional absorption in the far-infrared range.

### 3.2. The Gaseous Collision-Induced Absorption

Figure 4 is a schematic diagram showing the possible collisional interactions between the molecular species included in the model ($\text{H}_2$, $\text{N}_2$, $\text{CH}_4$, and $\text{Ar}$), which can give rise to a significant absorption in the spectral range of interest, between 180 and 640 cm$^{-1}$. Among the 10 possible binary interactions, we need to consider only 8 of them. Indeed, the $\text{Ar-}\text{Ar}$ pairs do not give rise to any infrared absorption for reasons of symmetry, and the $\text{H}_2-\text{H}_2$ absorption is made negligible by the low value of the $\text{H}_2$ mole fraction (~0.1%). Figure 5 shows the absorption spectra computed for the eight molecular pairs below 800 cm$^{-1}$, with the following assumptions on composition and temperature: $[\text{N}_2] = 0.898$, $[\text{Ar}] = 0.05$, $[\text{CH}_4] = 0.05$,

\[ \begin{align*}
    \text{H}_2-\text{N}_2 & \quad \text{H}_2-\text{CH}_4 \\
    \text{H}_2-\text{CH}_4 & \quad \text{N}_2-\text{CH}_4 \\
    \text{H}_2-\text{Ar} & \quad \text{N}_2-\text{Ar} \\
    \text{N}_2-\text{N}_2 & \quad \text{N}_2-\text{CH}_4 \\
    \text{N}_2-\text{Ar} & \quad \text{CH}_4-\text{CH}_4 \\
    \text{CH}_4-\text{Ar} & \quad \text{CH}_4-\text{Ar} \\
    \text{N}_2-\text{Ar} & \quad \text{N}_2-\text{Ar} \\
    & & \end{align*} \]

**FIG. 5.** Collision-induced absorption coefficients modeled for the interacting pairs shown in Fig. 4 (except the $\text{H}_2-\text{H}_2$ component which can be neglected) for an assumed mixture composition ($f_{\text{H}_2} = 0.05$, $f_{\text{CH}_4} = 0.05$, and $f_{\text{Ar}} = 0.002$) and a temperature of 80 K. The transitions of the $\text{H}_2-\text{Ar}$ dimers are also neglected.
$[\text{H}_2] = 0.002$, and $T = 80$ K. The details of the modeling of each component are given below.

$N_2$–$N_2$ and $N_2$–Ar pairs. We have used the semiempirical model of Courtin (1988). Below 100 cm$^{-1}$, absorption arising from these interactive pairs is the dominant one. However, these components, which peak near 60 cm$^{-1}$, rapidly decrease toward higher frequencies, and their contributions to the total absorption in the IRIS bandpass become very weak (less than 1%). Therefore, the use of existing ab initio models is not required.

$\text{CH}_4$–$\text{CH}_4$ and $\text{CH}_4$–Ar pairs. For the $\text{CH}_4$–$\text{CH}_4$ absorption, we have used the ab initio model of Borysow and Frommhold (1987). In the case of the $N_2$–Ar absorption (Courtin 1988), we have found that a simple scaling of the pure $\text{CH}_4$ absorption provided a good fit to the $\text{CH}_4$–Ar absorption measured in the laboratory by Dore and Fila- bozzi (1990) between 195 and 296 K. The scaling factor in this case is 0.6. This procedure has its justification in the fact that the absorption spectrum due to $\text{CH}_4$–Ar interactions is analogous to the transition spectrum of pure $\text{CH}_4$, with the notable difference that the double transition spectrum is obviously absent in the $\text{CH}_4$–Ar case (Dore and Fila- bozzi 1990). Because the influence of the double transitions is only important in the high frequency part of the spectrum—where $N_2$–$\text{CH}_4$ and $H_2$–$N_2$ absorptions in Titan’s atmosphere are much larger—the error introduced by this simplification in our modeling of Titan’s thermal radiation is negligible.

$N_2$–$\text{CH}_4$ pairs. This interaction is expected to be the dominant one in the 100- to 500-cm$^{-1}$ interval. Yet in the past, its modeling has been the least accurate because of the lack of an ab initio model and because laboratory measurements available for semiemipirical modeling were scarce. Recent experimental as well as theoretical work by Birchbaum et al. (1993) and by Borysow and Tang (1993) have filled this important gap. We have used the ab initio model of the latter authors. A comparison with the semiepipirical model of Courtin (1988), used in previous studies of Titan’s infrared spectrum (Toon et al. 1988, McKay et al. 1989), shows that the two models diverge significantly only beyond 300 cm$^{-1}$ for temperatures relevant to Titan’s atmosphere. The absorption resulting from the ab initio model is decreasing much less rapidly than in the semiepipirical calculation, in agreement with the laboratory measurements. The discrepancy between the semiepipirical model and the previous data set of Dagg et al. (1986) had already been recognized by Toon et al., and it prompted them to introduce an adjustment (linear, between 1.0 and 1.75, from 200 to 300 cm$^{-1}$ and constant beyond). In retrospect, we find that their adjustment was not spectrally well suited: It was slightly overestimated (by up to 40%) between 200 and 350 cm$^{-1}$ and underestimated beyond 350 cm$^{-1}$ (by a factor of several at 500 cm$^{-1}$). Consequently, compared with theirs, our Titan models have less gaseous opacity below 350 cm$^{-1}$ and more above.

$H_2$–$N_2$ pairs. We have used the ab initio model of Borysow and Frommhold (1986a), which includes the transitions of the bound $H_2$–$N_2$ system. In Fig. 6, their theoretical spectrum is compared with two sets of laboratory spectra obtained at low temperatures ($T \sim 80$ K) in the $S(0)$ and $S(1)$ rotational lines of $H_2$. The experimental data sets are from Borch et al. (1988) and from McKellar (Personal communication 1990). The first set, obtained at a resolution of 0.5 cm$^{-1}$, has been recalibrated using the values measured by McKellar at 354 and 587 cm$^{-1}$ as reference points, and both sets have been convolved with the IRIS apparatus function (resolution 4.3 cm$^{-1}$). The relative agreement between the contrast of the dimer features observed in the two independent experiments is excellent. We also note that the structure is very similar for both lines, which should help in the identification of features not associated with the $H_2$–$N_2$ dimers in the IRIS spectra.

The model predictions are in good agreement at the center of each band and in the wings. However, the theoretical dimer features are slightly more pronounced than the observed ones. This could be a consequence of the isotropic potential approximation used by Borysow and Frommhold. We have corrected the predicted absorption slightly at each frequency step to match the contrast observed in the laboratory experiments. The correction factor, which ranges from 0.80 to 1.05, is assumed to be independent of temperature. In Titan’s atmosphere, the temperature range corresponding to the layers probed by
IRIS is roughly 70–95 K, therefore not much different from the conditions of the laboratory experiments. The error introduced by the temperature-independent adjustment should thus be quite small. The experimental data shown here correspond to mixtures containing equilibrated fractions of ortho- and para-H\textsubscript{2} at the given temperature. Similar data are available for normal H\textsubscript{2} (the ortho-to-para ratio is equal to 3). This will allow us to assert a possible departure of the ortho-to-para ratio from equilibrium.

\( H_2 - CH_4 \) pairs. We have used the \textit{ab initio} model of Borysow and Frommhold (1986b), which includes the transitions of the bound H\textsubscript{2}–CH\textsubscript{4} system. To our knowledge, there are no published laboratory measurements of the H\textsubscript{2}–CH\textsubscript{4} dimer transitions. The contribution of these transitions to the observed Titan features is expected to be at least an order of magnitude smaller than that of the H\textsubscript{2}–N\textsubscript{2} dimers. Possible inaccuracies in the \textit{ab initio} model should not have any significant impact on our study.

\( H_2 - Ar \) pairs. We have used a semiempirical model derived from the work of Courtin (1988) to fit the 5 cm\textsuperscript{-1} resolution measurements of Dore \textit{et al.} (1988) at 195 and 298 K, neglecting the fine structure arising from the bound H\textsubscript{2}–Ar system. Although these dimer transitions have been observed in the laboratory (McKellar, Personal communication 1990), they are not expected to contribute significantly to the observed features on Titan, at least at the spectral resolution of the IRIS instrument.

3.3. Cloud and Haze Opacities

The cloud and haze particles are treated as spherical Mie scatterers. The optical properties for condensed methane and haze material in our model are the same as those used by Toon \textit{et al.} (1988) and McKay \textit{et al.} (1989), respectively. The real part of the index of refraction for liquid methane is assumed to be 1.27, while the imaginary part is the one shown in Fig. 2 of Toon \textit{et al.} The cloud opacity is controlled by two parameters: the total optical depth at 200 cm\textsuperscript{-1} wavenumber, \( \tau_{\text{cloud}} \), and the mean radius of the droplets, \( r_{\text{cloud}} \). For the haze material, we assumed optical properties similar to those of laboratory synthesized "Titan tholins" (Khare \textit{et al.} 1984). The real part of the index of refraction is equal to their measured values, whereas the imaginary part is scaled from their data set using the parameter \( \alpha_{\text{haze}} \). Figure 7 represents the spectral variations of the cloud and haze opacities in the 180- to 640 cm\textsuperscript{-1} range. The cloud opacity, corresponding to four values of the mean particle radius \( r_{\text{cloud}} = 10, 30, 50, \) and 100 \( \mu \text{m} \), is normalized to a value of 0.1 at 200 cm\textsuperscript{-1}. The haze opacity is calculated assuming a scaling factor \( \alpha_{\text{haze}} = 1.0 \).

![FIG. 7. Optical thicknesses calculated for cloud particles of radius ranging from 10 to 100 \( \mu \text{m} \) (top curves) and for a haze model adopted from McKay \textit{et al.} (1989) (bottom curve). For sizes comparable to the wavelength, the cloud particles act mostly as scatterers (Mie regime), and the size effect is dominant. Here, the optical thicknesses are normalized to 0.1 at 200 cm\textsuperscript{-1}. The haze particles are absorbers/emitters (Rayleigh regime), and the optical thickness is proportional to the total quantity of material times the imaginary index of refraction. Here, we assumed a refraction index equal to that of laboratory tholins.]

### 4. MODEL CASES

Each case is described by a set of seven parameters (see the parameter values listed in Table I): \( f_{H_2}, f_{Ar}, H_{\text{CH}_4}, S_{\text{CH}_4}, \tau_{\text{cloud}}, \rho_{\text{cloud}} \), and \( \alpha_{\text{haze}} \). In the case where the CH\textsubscript{4} distribution is constant with altitude, \( H_{\text{CH}_4} \) and \( S_{\text{CH}_4} \) are simply replaced by \( f_{\text{CH}_4} \). We have attempted to reproduce the IRIS data sample by adjusting the parameters listed above and by making various assumptions regarding the structure of Titan's atmosphere. We started with two simple models, one with only gaseous and haze opacities (labeled "no cloud"), and another including the influence of a tropospheric CH\textsubscript{4} condensation cloud (labeled "distributed cloud").

#### 4.1. The No Cloud and Distributed Cloud Cases

In both cases, the argon mole fraction is zero, and the methane distribution is limited by saturation. At the

#### TABLE I

<table>
<thead>
<tr>
<th>Model</th>
<th>Name</th>
<th>( f_{H_2} )</th>
<th>( f_{Ar} )</th>
<th>( H_{\text{CH}_4} )</th>
<th>( S_{\text{CH}_4} )</th>
<th>( \tau_{\text{cloud}} )</th>
<th>( \rho_{\text{cloud}} (\mu \text{m}) )</th>
<th>( \alpha_{\text{haze}} )</th>
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<td>1</td>
<td>No cloud</td>
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<td>—</td>
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<td>0.00</td>
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<td>50</td>
<td>0.85</td>
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<td>50</td>
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<td>0.00</td>
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<td>50</td>
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<tr>
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<td>—</td>
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<td>0.60</td>
<td>2.70</td>
<td>—</td>
<td>—</td>
<td>0.45</td>
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</table>

* Corresponding to a constant mole fraction of 4%.
surface, the relative humidity of methane is 60%. This leads to a CH₄ mole fraction of 6.6% from the surface up to the condensation level around 5 km and to a stratospheric mole fraction of 1.7%. The value of $H_{CH_4} = 0.60$ was adopted from the work of Toon et al. (1988). We find that varying that parameter between 0.4 and 0.8 produces a variation in brightness temperature of less than 0.5 K in the 450- to 550-cm⁻¹ interval. In other words, that parameter is only weakly constrained by the thermal emission spectrum. The only other constraint comes from Flasar (1983) who found that stability conditions in the bottom few kilometers impose $H_{CH_4} \approx 0.70$. In all subsequent models, we therefore used a value of 0.60. The normalized weighting functions calculated at 200, 300, 400, 500, and 600 cm⁻¹, for these two atmospheric models are shown in Fig. 8. These functions are defined as

$$W(z) = e^{-\tau(z)} \times H \times \frac{\partial \tau(z)}{\partial z},$$

where $\tau(z)$ is the optical depth as a function of altitude $z$, $\mu$ is the cosine of the viewing angle, and $H$ is the atmospheric scale height.

Figure 8a corresponds to the no cloud case, and Fig. 8b to the distributed cloud case. In the no cloud case, the weighting functions peak in the lower troposphere, the altitude of maximum contribution decreasing steadily from 20 to less than 5 km as the wavenumber increases from 200 to 600 cm⁻¹. On the other hand, the stratospheric contribution increases dramatically above 400 cm⁻¹, as noted by Toon et al. (1988). In the distributed cloud case, the altitudes of the maxima are raised significantly, ranging between 7 and 22 km, and there is a sharper decrease at the top of the cloud near 30–35 km. Another important difference between the two cases concerns the contribution of the surface to the outgoing radiation, as shown in Fig. 9. Whereas in the no cloud case a wide atmospheric window exists between 420 and 560 cm⁻¹, it is almost totally suppressed in the distributed cloud case.

Figure 10 shows the calculated brightness temperature spectrum corresponding to the above cases in the 180- to 640-cm⁻¹ range, compared with the IRIS data sample. Clearly, it is not possible to adjust the no cloud case parameters to match the IRIS measurements at all frequencies: $f_{H_2}$ and $\alpha_{H_2}$ are constrained by fitting the radiance at 355 and 585 cm⁻¹, and $H_{CH_4}$ has only a very minor influence on the calculated spectrum. In the distributed cloud case, a better match is obtained in the 400- to 600-cm⁻¹ interval by adjusting the cloud optical thickness, leading to values of $\tau_{cloud} \approx 4.0$. Still, an important mismatch subsists below 350 cm⁻¹. The only yet uncon-

![FIG. 8. Normalized weighting functions and thermal profile calculated for the no cloud case (a) and the distributed cloud case (b) at 200, 300, 400, 500, and 600 cm⁻¹.](image)

![FIG. 9. Surface contribution to the total thermal emission in the no cloud case (solid line) and the distributed cloud case (dashed line). The atmospheric window present in the former case is almost totally suppressed when a thick CH₄ condensation cloud is included.](image)
strained model parameter is the mean particle radius (the spectrum shown in Fig. 10 corresponds to \( r_{\text{cloud}} = 50 \mu m \)). To improve the agreement with the IRIS data, we would need to increase the cloud opacity between 200 and 350 cm\(^{-1}\) by almost one order of magnitude without changing its value between 400 and 550 cm\(^{-1}\) significantly. A value of \( r_{\text{cloud}} \) of 50 \( \mu m \) already implies that the opacity at 200 cm\(^{-1}\) is about twice that at 450 cm\(^{-1}\). For values of \( r_{\text{cloud}} \) smaller than about 40 \( \mu m \), the opacity at 400–500 cm\(^{-1}\) becomes larger than that at 200 cm\(^{-1}\) (see Fig. 7). Thus, decreasing \( r_{\text{cloud}} \) makes the discrepancy with the IRIS data even worse, until the particle radius reaches a fraction of 1 \( \mu m \), in which case matching solutions do exist. That type of solution had been proposed earlier by Thompson and Sagan (1984), but Toon et al. (1988) presented strong arguments against it, mainly the fact that the cloud optical depth in the visible would be so large that it would block all sunlight and make the observed greenhouse impossible to explain. Increasing \( r_{\text{cloud}} \) to 100 \( \mu m \) and above has a negligible effect, since the cloud opacities at 200–350 and 400–500 cm\(^{-1}\) stay about equal. Thus, no distributed cloud model can reproduce the IRIS data accurately. The basic reason is that the weighting functions at 200–350 cm\(^{-1}\) peak too low in the troposphere.

We also calculated the hydrogen dimer spectra corresponding to the above cases. The comparison is shown in Fig. 11a, for the \( S(0) \) line, and in Fig. 11b, for the \( S(1) \) line. The computation in the \( S(0) \) line predicts too much contrast in comparison with the observations. This confirms the idea that additional background opacity, independent of the \( H_2 \) mole fraction, is needed at 350 cm\(^{-1}\) and below. In the \( S(1) \) line, the no cloud case best matches the observed contrast. However, the overall agreement is rather poor in both cases. As noted at the end of Section 2, this is partly explained by the fact that extra features not associated with the hydrogen dimers seem to be present in that region of the spectrum. We will defer the discussion of this problem to the end of Section 4.2.

4.2. The Cold Cloud, Supersaturation, and Constant \( CH_4 \) Cases

There are two possible ways of solving the discrepancies noted above: Either by arbitrarily moving the cloud upward to a colder level, thus partially blocking the mid-tropospheric radiation, or by increasing the gas opacity in the 15- to 30-km altitude range, the layers which mostly contribute to the spectral interval between 200 and 300 cm\(^{-1}\). In the latter case, the only solution is to increase the methane mole fraction in the condensation region, thus allowing supersaturation.

We have investigated these possibilities by devising three types of models, namely a "cold cloud" case, a "supersaturation" case, and a "constant \( CH_4 \)" case. We also tested "intermediate" cases, where the first two solutions are combined (see parameter values in Table 1). Figure 12 represents the normalized weighting functions for the three cases. Figure 12a corresponds to the cold cloud case that produces the best agreement. We found that the cloud needs to be located very near the temperature minimum around 40 km, with an optical thickness at 200 cm\(^{-1}\) of 0.75. Its vertical extent does not affect the computed emission in any significant way, provided that the peak of the weighting function is located near the minimum temperature. For simplicity, we have reduced the cloud extent to a single model layer, which results in the artificially sharp peaks seen in Fig. 12a. As expected, the contribution from the tropopause is strongly increased at all frequencies, the outgoing radiation then being the sum of that contribution and that from the lower troposphere. In the supersaturation case, we found the best agreement with a value \( S_{CH_4} = 2.0 \), with a cloud opacity set to zero. The "intermediate 1" and "intermediate 2" cases have cloud opacities of 0.4 and 0.2 and supersaturation factors of 1.4 and 1.7, respectively. The weighting functions of the supersaturation case, shown in Fig. 12b, are quite similar in shape to those of the no cloud case, except that at 200, 300, and 400 cm\(^{-1}\), they are raised a few kilometers and somewhat widened. For the constant \( CH_4 \) case, we find the best fit with a mole fraction of 4%.

The weighting functions, shown in Fig. 12c, are still higher at 200 and 300 cm\(^{-1}\) and broader at all frequencies.

Figure 13 shows the relative contribution from the surface in the three above cases. In this respect, there is no fundamental difference between these cases since a wide atmospheric window exists in all three. Compared with the no cloud case (see Fig. 9), the surface contribution in the three new cases is increased because the \( H_2 \) mole fraction, and hence the gas opacity in the window, has decreased. Moreover, the magnitude of the surface emis-
FIG. 11. Comparison between the IRIS-observed dimer features and the predictions of the no cloud case (solid line) and the distributed cloud case (dashed line), in the S(0) (a) and S(1) (b) lines.

FIG. 12. Same as Fig. 8 for the cold cloud case (a), the supersaturation case (b), and the constant CH₄ case (c).

Emission is largest in the constant CH₄ case because of a much lower CH₄ concentration in the bottom layers.

Figure 14 shows the corresponding emission spectra compared with the IRIS data sample in the 200- to 600-cm⁻¹ interval. The agreement is excellent in the first two cases, but slightly poorer in the constant CH₄ case. There is too little absorption around 400–450 cm⁻¹ and too much around 200–300 cm⁻¹. This could be an indication that the methane distribution indeed varies with altitude. Alternatively, this could mean that the tropopause tempera-
ture is warmer than derived from the radio occultation data when argon is neglected and the discrepancy at 200–300 cm\(^{-1}\) would constitute an indirect signature of argon in Titan's atmosphere. However, no firm conclusion concerning the presence of argon may be drawn at this stage of our modeling.

To discriminate among the various possible solutions, we also computed the associated hydrogen dimer spectra which are shown in Fig. 15a, for the S(0) line, and Fig. 15b, for the S(1) line. In the S(0) line, the cold cloud and supersaturation cases give an equal fit to the data, whereas the agreement is rather poor in the constant CH\(_4\) case. Below about 345 cm\(^{-1}\), the computed brightness temperatures are slightly lower than the measurements. This can be explained by the fact that we have neglected the stratospheric emission in the C\(_2\)H\(_2\) band centered at 328 cm\(^{-1}\). The contribution from the \(R\) branch extends from 331 to 345 cm\(^{-1}\) and is maximum around 337 cm\(^{-1}\) (Kunde and Courtin 1989). In the S(1) line, the agreement is best for the supersaturation and the constant CH\(_4\) cases. In the cold cloud case, the discrepancy is due to the fact that the haze emission needs to be increased to the point where the contrast in the dimer features is strongly depressed, and the slope of the spectrum is modified. Nevertheless, the \(rms\) of the brightness temperature residuals is only of the order of twice the NET\(_B\) of the IRIS data sample. That case is thus marginally acceptable. Among the intermediate cases (not shown in Fig. 15), those corresponding to CH\(_4\) saturation ratios above 1.4 produce an agreement close to that obtained with the supersaturation case.

There are several features in the S(1) line that cannot be reproduced within the 3\(\sigma\) instrumental noise level, near 576 cm\(^{-1}\), near 595 cm\(^{-1}\), and in the 602- to 610-cm\(^{-1}\) interval. Unlike in the case of the S(0) line, these discrepancies can hardly be explained by the influence of identified stratospheric emission lines. The \(P\) branches of the C\(_2\)H\(_2\) and C\(_3\)H\(_4\) bands centered, respectively, at 638 and 633 cm\(^{-1}\) contribute very little emission below 610 cm\(^{-1}\). One could question the accuracy of the modeling of the dimer transitions. However, the fact that the two independent spectroscopic measurements of Bachet et al. (1988) and McKellar (Personal communication 1990) agree remarkably well with each other strongly reinforces our confidence in the idea that these features are not associated with the H\(_2\) dimers. As a check, we calculated spectra using the uncorrected \(ab\) \(initio\) coefficients of Borysow and Frommhold (1986). Although faint features appear in that case at 576 and 597 cm\(^{-1}\), they do not provide a good match to the observed ones. Therefore, we suggest that these excess brightness features are due to stratospheric emission lines from one or several unidentified atmospheric constituents. For instance, H\(_2\)O does possess a weak transition near 576 cm\(^{-1}\). However, the identification of that feature with a water vapor (or water ice) line is not consistent with the fact that stronger lines in the same wavelength range are not seen in the IRIS data.

4.3. Constraints Derived from the Intensity Ratio

To lift the ambiguity between the three previous models, further constraints can be derived from limited measurements of the intensity ratio, which is defined as the quantity

\[
[I_o(\theta_2) - I_o(\theta_1)]/I_o(\theta_2),
\]

where \(I_o(\theta)\) is the radiation intensity corresponding to the emission angle \(\theta\). The IRIS instrument recorded two sequences of spectra at close locations on Titan with emission angles of 52.7° (29 spectra) and 7.3° (10 spectra), respectively. The intensity ratio resulting from these measurements is shown in Fig. 16, along with those computed
for the three models described in Section 4.2. Clearly, the constant CH$_4$ case can be definitely rejected because of the mismatch of the intensity ratio in the 300- to 400-cm$^{-1}$ range. This discrepancy stems from the low opacity in the bottom 10 km of that model. The supersaturation and cold cloud cases give reasonable fits up to about 500 cm$^{-1}$. Above that, they both predict intensity ratios that are too high, but still within the 2σ limit. Therefore, both models are considered adequate in terms of matching the IRIS data set and both will be used for subsequent sensitivity studies.

4.4. Sensitivity Studies

In the following, we retain the cold cloud and supersaturation cases as two extreme plausible models in order to bracket the values of the H$_2$ mole fraction, $f_{H_2}$, the mean radius of the cloud particles, $r_{cloud}$, and to determine an upper limit on the argon mole fraction, $f_{Ar}$.

4.4.1. The H$_2$ mole fraction. For each type of model, we varied $f_{H_2}$, leaving all other parameters unchanged, and computed the S(0) and S(1) hydrogen dimer spectra. Using a least-mean-square procedure, we slightly shifted the calculated spectra to obtain the best overall fit in each line. We then computed the variance $\sigma^2_\beta$ of the brightness temperature residuals between 340 and 380 cm$^{-1}$ in the S(0) line and between 560 and 600 cm$^{-1}$ in the S(1) line. These limits were chosen so as to minimize the systematic bias caused by the stratospheric emission bands mentioned in Section 4.2. For the supersaturation case, Figs. 17a and 17b show how the fit to the IRIS data in the S(0) and S(1) lines varies when the hydrogen mole fraction varies from $6 \times 10^{-4}$ to $2 \times 10^{-3}$. For each case, we also calculated a parameter indicating the goodness of the fit, defined as

$$\chi^2 = \sigma^2_\beta/\text{NET}_\beta.$$

The variations of $\chi^2$ as a function of the H$_2$ mole fraction are shown in Fig. 18a (supersaturation case) and Fig. 18b (cold cloud case). The goodness of the fit can be directly appreciated from these curves. In the supersaturation case, the $\chi^2$ of the S(0) line shows a pronounced minimum of 1.4 for $f_{H_2} = 1.3 \times 10^{-3}$, whereas for the S(1) line it shows only a shallow minimum of 2.0 centered around $1.0 \times 10^{-3}$. In the cold cloud case, only the $\chi^2$ of the S(0) line exhibits a minimum of 3.3 around $0.8 \times 10^{-3}$, whereas that of the S(1) decreases asymptotically toward the same value, but for larger values of the H$_2$ mole fraction. This reflects the impossibility for this model to match both lines accurately with the same value of $f_{H_2}$. Because of the relatively poor fits obtained in the S(1) line, which may
be due to unidentified emission bands, and also because of the lack of sensitivity of that line to variations of $f_{H_2}$, we chose to base our determination only on the fits of the $S(0)$ line for both models. The supersaturation case leads to $f_{H_2} = 1.3 \pm 0.3 \times 10^{-3}$, whereas the cold cloud case leads to $0.8 \pm 0.3 \times 10^{-3}$. The error bars are calculated from the second derivative of the $\chi^2$ curve (Bevington 1969):

$$\delta f_{H_2} = \sqrt{\frac{2}{\delta f_{H_2}^2 \chi^2}}.$$  

Combining the two determinations yields $f_{H_2} = 1.0 \pm 0.4 \times 10^{-3}$. Although it is much more inaccurate, the determination based on the $S(1)$ line in the supersaturation case agrees well with this mean value. It is worth noting that our determination is based on the simultaneous fit of the absolute brightness temperature and of the observed contrast in the hydrogen dimer transitions. Thus, it is fairly robust with respect to the assumed additional background opacity. Consequently, all subsequent models, in particular those containing argon, should also be characterized by a mole fraction of $H_2$ that is consistent with the above determination. This may be used to constrain the abundance of argon.

The above study was carried out under the assumption that the ortho-to-para ratio is determined by equilibrium at the local temperature. We also ran a case in which the ortho-to-para ratio was set to its high-temperature limit of 3. A marginal fit was obtained with a value of $f_{H_2}$ about twice as large and a slightly higher supersaturation ($S_{CH_4} = 2.7$). However, the agreement is worse than in the equilibrated case, and the computed intensity ratio is too large at all frequencies, so we conclude that there is no evidence for a departure from equilibrium.

**FIG. 18.** Variations of the "goodness of fit" parameters $\chi^2$ in the $S(0)$ and $S(1)$ lines as a function of $f_{H_2}$, for the supersaturation case.
4.4.2. The cloud particles mean radius. The cold cloud case can be further characterized by constraining the mean radius of the cloud particles through its influence on the spectral shape of the cloud opacity. In Fig. 19, we compare spectra computed with various values of \( r_{\text{cloud}} \) between 40 and 100 \( \mu \text{m} \), all other parameters being unchanged. The best agreement is obtained for values between 50 and 60 \( \mu \text{m} \), which correspond to the requirement that the cloud opacity be minimal in the 400- to 500-cm\(^{-1}\) interval. For values outside that interval, the cloud becomes too opaque between 300 and 500 cm\(^{-1}\). Furthermore, it is not possible to maintain a good agreement by changing the values of the \( \text{H}_2 \) mole fraction and of the haze emissivity. Even marginal fits can be obtained only with values of these parameters that are not compatible with the observed contrast of the dimer features.

In principle, the uncertainty on the mean radius of the cloud particles should propagate into the determination of the mole fraction of \( \text{H}_2 \), since it influences the emission in the \( S(0) \) line. However, the contrast of the dimer features in the \( S(0) \) line, on which the determination of the \( \text{H}_2 \) mole fraction is based, is only very weakly dependent on variations of the mean radius within the bounds given above. Therefore, we think it is justified to consider them as independent parameters.

4.4.3. The argon mole fraction. Based on the supersaturation case (referred here as "argon 0" case), we have derived two models in which the mole fraction of argon is increased to 0.05 ("argon 1" case) and 0.10 ("argon 2" case), respectively. We have also considered models similar to the cold cloud case to check the sensitivity of our method for the determination of an upper limit for \( f_{\text{Ar}} \). The main influence of the inclusion of argon in the model is on the \( S(0) \) line, where both types of model produce very similar fits. Therefore, the constraint on the argon mole fraction should be largely independent of the assumed background opacity model.

We have used the following method: First, the thermal emission is computed between 180 and 640 cm\(^{-1}\) with model parameters adjusted to produce a good fit of the broadband IRIS data, especially in the vicinity of the \( \text{H}_2 \) lines. In particular, this sets the value of \( f_{\text{H}_2} \) as a function of \( f_{\text{Ar}} \). Then, the contrast of the dimer transitions is calculated in both lines, and the least-square method used previously is repeated to calculate \( \chi^2 \) values as a function of \( f_{\text{Ar}} \).

As a consequence of the warmer temperature profile implied by the higher argon mole fraction, maintaining the agreement requires increasing the methane mole fraction in the troposphere, thus increasing the supersaturation parameter \( S_{\text{CH}_4} = 2.25 \) and \( 2.50 \), respectively), and decreasing the hydrogen mole fraction \( f_{\text{H}_2} = 8 \times 10^{-4} \) and \( 5 \times 10^{-4} \), respectively). Conversely, the haze infrared emissivity needs to be decreased \( (\alpha_{\text{haze}} = 0.35 \text{ and } 0.20, \text{ respectively}) \). Figure 20 shows that excellent fits of the IRIS data sample can be obtained with such argon-containing models. In the absence of any other constraint, it would not be possible to improve on the existing upper limit of argon. However, because the \( \text{H}_2 \) mole fraction required to fit the absolute brightness temperature decreases as argon increases, the contrast of the hydrogen dimer features (shown in Figs. 21a and 21b) also decreases significantly. For the argon 1 case, the contrast in the \( S(0) \) line appears compatible with that measured by IRIS, but it is definitely too weak for the argon 2 case. In the \( S(1) \) line, both argon-containing models are marginally compatible with the measured contrast. Figure 22 shows the variation of the \( \chi^2 \) values as a function of \( f_{\text{Ar}} \). As noted above, it is much more sensitive in the \( S(0) \) than in the
S(1) line. The reason is that in the S(1) line, background emission from the haze strongly attenuates the contrast variations, whereas in the S(0) line, H$_2$ contributes for a large part to the total opacity.

Clearly, models with very low concentrations of argon give a better agreement with the observations. Using an estimate of the second derivative of the S(0) line $\chi^2$ curve in the range 0.00 $\leq f_{Ar} \leq$ 0.05, we find an upper limit for the argon mole fraction of 0.02 (1$\sigma$). That upper limit should be largely insensitive to the type of tropospheric opacity we assumed. We checked that statement by computing similar argon models based on the cold cloud case. Although the agreement with the broadband spectrum is worsened, the residuals in the H$_2$ lines are quite comparable to those shown in Fig. 22, leading to the same upper limit. Given the somewhat indirect nature of the procedure used to derive that upper limit—based on the simultaneous fit of the absolute emission in the H$_2$ lines and of the contrast of the H$_2$--N$_2$ dimer features and not on any direct spectroscopic effect due to argon itself—we feel that it is more appropriate to set the upper limit at the 3$\sigma$ level, that is $f_{Ar} \leq$ 0.06.

We further tested the argon 1 and argon 2 cases against the intensity ratio data. These models produce a good or marginal agreement, the best fit being obtained with the argon 1 case (see Fig. 22). Above 400 cm$^{-1}$, the intensity ratio is highly sensitive to the relative stratospheric contribution, which is on the haze emissivity. Values of $\alpha_{haze}$ between 0.30 and 0.50 seem to be preferred. Indirectly, this tends to favor models with a nonzero argon mole fraction, which are characterized by lower values of $\alpha_{haze}$. Given the rather large uncertainties associated with the intensity ratio above 400 cm$^{-1}$, it is probably premature to conclude that the presence of argon is necessarily required.

5. SUMMARY OF RESULTS AND DISCUSSION

5.1. Summary of Results

The broad characteristics of Titan’s thermal spectrum between 200 and 600 cm$^{-1}$ can be matched with many different models. However, a definite conclusion is that a continuum absorption is needed in addition to the expected collision-induced gas opacity. There are two possible sources for that opacity: either a condensation cloud or a methane distribution exceeding saturation in the troposphere. We find that models based on the latter assumption and containing very low concentrations of argon give the best agreement with all the observational constraints, while a marginal agreement is obtained with models in which a thin cloud is located at the temperature minimum. In addition to the broadband thermal spectrum character-
sorption in our model, not only that of the $\mathrm{H}_2$–$\mathrm{N}_2$ pairs, but most importantly of the $\mathrm{N}_2$–$\mathrm{CH}_4$ pairs. The photochemical model of Yung et al. (1984) predicts a $\mathrm{H}_2$ mole fraction of $2.1 \times 10^{-3}$, but a more recent calculation by Toubiana et al. (1995) gives a slightly lower value of $1.6 \times 10^{-3}$ that is in agreement with our findings.

To agree with the earlier determinations of the $\mathrm{H}_2$ mole fraction, Yung et al. had invoked the catalytic recombination of $\mathrm{H}$ into $\mathrm{H}_2$. However, the model of Toubiana et al. suggests that this mechanism is quite inefficient at modifying the $\mathrm{H}_2$ mole fraction in the bulk of the atmosphere. On the opposite, the present determination may be suggestive of other processes tending to inhibit the formation of molecular hydrogen in Titan's atmosphere or leading to a stronger escape of hydrogen than currently considered.

5.2.2. The abundance of argon. It is well known that the atmosphere of Titan is not of primary origin. If that were the case, the $\mathrm{Ne}/\mathrm{N}$ ratio would be close to unity, leading to a mean molecular mass inconsistent with observation (Owen 1982). A secondary origin is then required. Lunine and Stevenson (1985) quantified the noble gas composition of Titan under two main hypotheses. If $\mathrm{N}_2$ was entirely derived from clathrates embedded in the saturnian subnebula, the $\mathrm{Ar}/\mathrm{N}_2$ ratio would be between 0.01 and 0.1. If $\mathrm{N}_2$ was formed via photochemistry or shock-heating from a primitive $\mathrm{NH}_3$ atmosphere—which would imply a saturnian subnebula containing nitrogen mainly in the form of $\mathrm{NH}_3$ gas and ice, as advocated by Prinn and Fegley (1981)—then $\mathrm{Ar}/\mathrm{N}_2$ would be much less than 0.01. Unfortunately, the present result does not permit us to discriminate between the two scenarios.

On the other hand, laboratory measurements show that forming clathrates at temperatures and pressures expected to have occurred in the saturnian subnebula is not so easy (Bar-Nun et al. 1985). These authors suggest that more likely $\mathrm{N}_2$, $\mathrm{CH}_4$, and $\mathrm{Ar}$ were trapped by amorphous water ice embedded in the subnebula, and subsequently released in the atmosphere of Titan. However, they did not evaluate the resulting $\mathrm{Ar}/\mathrm{N}_2$ ratio.

Another possibility is that the atmosphere of the satellite originated from infalling comets formed from ices at 50 K in the Uranus–Neptune region of the solar nebula or at 30 K in the Kuiper belt (Zahnle and Dones 1992, Zahnle et al. 1992). Argon and nitrogen could have been trapped in such ices (Bar-Nun et al. 1988). More recently, Owen and Bar-Nun (1994) reanalyzed the problem: they conclude that infalling comets would have generated an atmosphere in which the $\mathrm{Ar}/\mathrm{N}_2$ ratio should not exceed a few percent. This prediction is consistent with our upper limit.

5.2. Discussion

5.2.1. The abundance of hydrogen. The abundance we find for $\mathrm{H}_2$ is significantly lower than previous determinations based on the IRIS spectra (Samuelson et al. 1981, Toon et al. 1988, Courtin et al. 1988). This is indeed a consequence of the updating of the collision-induced ab-
infrared, either with ground-based telescopes or with the Infrared Space Observatory (ISO) of the European Space Agency. Preliminary calculations, however, indicate that a detection with ISO would be possible only for argon mole fractions larger than about 10% (Courtois 1990). Thus, given the present upper limit of 6%, a nondetection would not be very conclusive. The situation in the near-infrared might be more favorable, but it is somewhat complicated by the presence of many CH$_4$ lines which are at the moment poorly modeled.

5.2.3. The distribution of methane. Condensation in Titan’s troposphere occurs as a mixture of CH$_4$ and N$_2$ and has been studied in some detail (Thompson 1985, Thompson et al. 1990, 1992, Kouvaris and Flasar 1991). Thus, the actual supersaturation of CH$_4$ is properly defined as the mixing ratio divided by the mixing ratio that would just begin formation of a CH$_4$ and N$_2$ condensate. In general the presence of N$_2$ reduces the mixing ratio at which CH$_4$ saturation occurs by 20% and the resulting condensate contains 20% N$_2$. To correct for this effect, all of the saturations reported here can be increased accordingly.

Our results clearly suggest the possibility that Titan’s troposphere is supersaturated with respect to CH$_4$ and that condensation may be absent altogether. We have used the model of Moses et al. (1992) for hydrocarbon condensation in the atmosphere of Neptune to investigate the plausibility of supersaturation of CH$_4$ and C$_2$H$_6$ on Titan. For supersaturation to persist requires that condensation be kinetically inhibited or that tropospheric transport is more efficient at resupplying CH$_4$ than rainfall is at removing it. Moses et al. (1992) suggest that, as a result of kinetic inhibition, CH$_4$ in Neptune’s atmosphere is supersaturated by 3 and C$_2$H$_6$ by factors of up to several hundreds. We have applied their method—based on classical condensation theory—to the case of CH$_4$ condensation on Titan. The method computes the rate of condensate formation as a function of supersaturation for various values of the contact angle. These results are shown in Fig. 24. Because the temperature in the region of saturation of CH$_4$ on Neptune and on Titan is similar (75 K), the only difference between the two cases is the size of the condensation nuclei. While Moses et al. (1992) used 10-nm particles, the haze particles in Titan’s troposphere are expected to be 150 nm (McKay et al. 1989). Thus, our Fig. 24 can be compared with Fig. 10a of Moses et al. to see the effect of a factor of 10 change in particle size.

There are two other major uncertainties in the application of classical condensation theory to Titan: (1) determining the value of the contact angle and (2) specifying the desorption energy required to remove a molecule from the surface. Moses et al. (1992) considered that for condensation of hydrocarbons onto an insoluble particle, the wetting angle would be greater than 45°, and we assumed likewise. For the desorption energy we also followed Moses et al. and used the value of 0.18 eV—the value for water on silicates—but changes by factors of 0.5 and 2.0 around that value produced less than 10% changes in the computed saturation ratio.

The contact angle is difficult to estimate but we note that the expected condensation nuclei—made of tholins—are insoluble in CH$_4$, C$_2$H$_6$, and other polar hydrocarbons (Raulin 1987). In such cases contact angles for the liquid condensation are typically larger than 40°–50° (Pruppacher and Klett 1978). In the upper atmosphere, the temperatures are below freezing and any condensation initiated here would be directly into the solid form. In this case even larger supersaturations are expected (Moses et al. 1992). In either case, the contact angle may indeed be greater than 40°–50° and, as the curves in Fig. 24 show, then supersaturations of more than two to three are sustained.

We have assumed that the condensation nuclei are tholins. It is possible that as the tholins enter the CH$_4$ saturation region, they have already been coated with a layer of C$_2$H$_6$—which reaches saturation in the lower stratosphere. However, the case for C$_2$H$_6$ is again similar to that on Neptune. If C$_2$H$_6$ did not condense in Titan’s atmosphere, its supersaturation would reach values of 500 at the tropopause. This is similar to the values that Moses et al. (1992) find for supersaturation of C$_2$H$_6$ on Neptune. Thus, we propose that condensation of C$_2$H$_6$ as well as CH$_4$ are significantly inhibited—and possibly completely suppressed—in Titan’s atmosphere. If condensation is occurring, it is likely to be in the troposphere where a condensed phase mixture of CH$_4$, C$_2$H$_6$, and N$_2$
should form. CH$_4$ condensation, if it occurs, would provide a compatible surface allowing C$_2$H$_6$ condensation. Because of its higher mixing ratio, CH$_4$ condensation is more likely to occur at lower supersaturations than that for C$_2$H$_6$ (Moses et al. 1992).

On the other hand, we note that a sink of C$_2$H$_6$ must exist at some altitude or at the surface; otherwise it will accumulate in the atmosphere as a result of the continuous photolysis of CH$_3$. If condensation is completely inhibited as suggested above then the sink for C$_2$H$_6$ would be deposition onto the surface. Alternatively, if C$_2$H$_6$ does condense in the lower stratosphere, then these condensation nuclei reaching the CH$_4$ saturation region are coated with a C$_2$H$_6$ surface and condensation should proceed at very low supersaturation. In this case, supersaturation can be maintained only if the transport of CH$_3$ by eddy diffusion—which tries to set a constant CH$_4$ mixing ratio—is more efficient than CH$_4$ removal by the falling particles. It is possible to estimate the eddy diffusion coefficient required to sustain a supersaturation of CH$_4$ by balancing the eddy transport upward with condensation onto tholin particles coated with C$_2$H$_6$. If the CH$_3$ particles grow to sizes of $\approx$100 $\mu$m (Toon et al. 1988), then a supersaturation of 2 in the upper troposphere would imply an eddy diffusion coefficient of $\approx 3 \times 10^4$ cm$^2$ sec$^{-1}$. Higher eddy coefficients would result in saturation closer to unity. However, in this scenario there would still be CH$_4$ condensation, the release of latent heat, and the concomitant affect on the temperature lapse rate.

We have considered the limiting case for the supersaturated hypothesis: Namely, no condensation of either CH$_4$ or C$_2$H$_6$ anywhere in Titan’s atmosphere. In this case, eddy mixing would tend to produce approximately constant mixing ratio profiles for these gases, with small gradients necessary to drive the upward flux of CH$_4$ and the downward flux of C$_2$H$_6$ required by photochemical balance. The source of CH$_4$ and the sink for C$_2$H$_6$ would be at the surface.

At the cold trap situated near 30 km altitude, we constrain the CH$_4$ mole fraction between 1.7 and 4.5%. Lellouch et al. (1989) derived an upper limit of 3.4% from the analysis of the CH$_4$ $\nu_2$ emission measured by Voyager IRIS. However, they did so under the assumption of saturation. When that condition is relieved, larger values of the stratospheric mole fraction are also compatible with the $\nu_2$ band emission. Therefore, our result is not inconsistent with theirs. More recently, Strobel et al. (1993) obtained a lower limit of 2.6% for the CH$_4$ mole fraction at the tropopause from the reanalysis of the Voyager UVS solar occultation measurements. From all the available estimates, one may conclude that the CH$_4$ mole fraction in Titan’s stratosphere should be in the range 2.6—4.5%.

5.2.4. The tropospheric cloud. The previous arguments for the presence of CH$_4$ clouds in Titan’s troposphere can be summarized as follows: (1) The level of CH$_4$ in the troposphere is such that a region of saturation will exist and condensation must therefore take place (see, e.g., Thompson et al. 1992). (2) It has been recognized that an additional source of thermal infrared opacity was needed in Titan’s troposphere to match the IRIS data (Samuelson et al. 1993) and clouds seemed a likely candidate. This study questions both these arguments. We find that the IRIS data require the suppression of condensation at some level and possibly the complete absence of clouds. Our model results in best agreement with the data do not contain a cloud. Titan’s troposphere may be free of clouds.

There are other indications that there are no clouds, or only very thin ones, in the troposphere of Titan. McKay et al. (1989) showed that radiative equilibrium models did not allow for a thick cloud but could not exclude the presence of an optically thin cloud ($\tau \leq 2$). Griffith et al. (1991) found that their observations of Titan in the 2- to 2.5-$\mu$m region were inconsistent with a global thick cloud cover. They placed an upper limit of 4% to the areal coverage by thick clouds located at 17–30 km. For any global cloud layer residing at the tropopause, they found an optical thickness of less than 0.1 at 2.16 $\mu$m. More recent observations in the 1- to 2-$\mu$m window from the ground (Lemmon et al. 1993), or near 1.0 $\mu$m with the HST WF/PC-2 camera (Smith et al. 1994), show albedo variations that must originate in the troposphere (clouds) or on the surface. The correlation of the albedo features with rotation argues against clouds as a significant source of albedo at 1–2 $\mu$m. Last, the lapse rate in the middle and upper troposphere, as determined from the Voyager data by Lellouch et al. (1989), is unstable with respect to moist convection, but stable with respect to dry convection. This has been explained by the averaging of regions with dry and moist lapse rates yielding an intermediate value, as occurs on Earth. Alternatively, if there was no condensation, the moist lapse rate would not apply and the observed radiative equilibrium profile would be self-consistent without invoking heterogeneous convection. Strictly speaking, of the scenarios presented here only the constant mixing ratio case should exhibit no condensation whatsoever.

5.2.5. The stratospheric haze. McKay et al. (1989) found that the optical properties of Titan’s haze layer required to fit the geometric albedo spectrum in the visible were similar in magnitude and slope to the optical properties of laboratory tholins. In particular they found that the absorptance of the laboratory tholins had to be multiplied by a constant factor of between 1.3 and 1.5 for best results. Because of this similarity in the visible, McKay et al. (1989) applied a scaling factor (0.5) to laboratory tholins to order to obtain the optical constants in the thermal infrared as well. We followed this approach and
have deduced a scale factor between 0.3 and 0.8. Thus, the optical properties needed to fit the spectrum are 0.3 to 0.8 times the measured laboratory tholins near 600 cm⁻¹. In both the visible and the thermal infrared the necessary optical properties are within a factor of ≈2 of that of the laboratory tholins, although in the visible the laboratory tholins are too bright, and in the thermal infrared they are too dark.

5.2.6. The surface temperature. Apart from its cosmogenic implications, the presence of argon in Titan’s atmosphere would imply slightly warmer surface temperatures than in the case of an atmosphere composed primarily of nitrogen and methane. For instance, for the cold cloud case, the surface temperature derived from the Voyager radio occultation data is 92.4 K, whereas for the argon case, it is 93.4 K. The warmest value, corresponding to the upper limit for argon, is 93.5 K. This has implications for the thermodynamics of a methane–ethane ocean, if such an ocean exists. We will not discuss these implications here, since they have been explored in detail by Dubouloz et al. (1989).

6. CONCLUSIONS

In closing, we comment that our analysis of the Voyager IRIS data has provided a new perspective on the possible nature of Titan’s troposphere. The general picture is that of virtually cloud-free layers supersaturated with CH₄, due to the low concentration of nuclei that are inefficient at nucleating the vapor phase. Clouds, if present, are probably more comparable to noctilucent clouds in Earth’s mesopause than to water clouds lower in the terrestrial atmosphere. Such a troposphere is probably inconsistent with any vigorous dynamical upwelling and downwelling. Thus, Titan’s troposphere may be very different from that of Earth—we suspect more quiescent, more uniform laterally, and with clouds that are thin if present at all. We may expect the Huygens probe, as it passes through this supersaturated region, to leave a trail of CH₄ condensate in its wake.

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