Methane, ethane, and mixed clouds in Titan’s atmosphere: Properties derived from microphysical modeling

Erika L. Barth a,∗, Owen B. Toon b

a Southwest Research Institute, 1050 Walnut St., Suite 400, Boulder, CO 80302, USA
b Program in Atmospheric and Oceanic Sciences and Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80309, USA

Received 7 August 2005; revised 14 December 2005
Available online 17 February 2006

Abstract

Theoretical arguments point to and recent observations confirm the existence of clouds in Titan’s atmosphere, yet we possess very little data on their particle size, composition and formation mechanism. A time-dependent microphysical model is used to study the evolution of ice clouds in Titan’s atmosphere. The model simulates nucleation, condensational growth, evaporation, coagulation, and transport of particles in a column of atmosphere. A variety of cloud compositions are studied, including pure ethane clouds, pure methane clouds, and mixed methane–ethane clouds (all with tholin cores). The abundance of methane cloud particles may be limited by the number of ethane coated tholin nuclei rather than the number of tholins with hydrocarbon coatings. However, even the condensation of methane onto these relatively sparse ethane/tholin cloud particles is sufficient to keep the methane close to saturation. Typical methane supersaturations are of order 0.06 on the average. For simulations which take into account recent lab measurements indicating it is relatively easy for methane to nucleate onto tholin particles without an ethane-layer present, the three types of clouds (methane, ethane, and mixed) exist simultaneously. Pure methane clouds are the most abundant cloud type and serve to lower the supersaturation to about 0.04. Cloud production does not require a continuous surface source of methane. However, clouds produced by mean motions are not the visible methane clouds seen in recent Cassini and ground-based observations. Ethane clouds in the troposphere almost instantaneously nucleate methane to form mixed clouds. However, a thin ethane ‘haze’ remains just above the tropopause for some scenarios and the mixed clouds at the tropopause remain ≤50% ethane by mass. Also, evaporation of methane from the mixed cloud particles near the surface leaves a thicker layer of ethane cloud particles at ∼10 km. Nevertheless, the precipitation rate of methane to Titan’s surface is between 0.001 and 0.5 cm/terrestrial-year, depending on various initial conditions such as critical saturation, size and abundance of cloud condensation nuclei, surface sources and eddy diffusion.

© 2005 Elsevier Inc. All rights reserved.

Keywords: Titan; Atmospheres, structure

1. Introduction

Titan, the largest satellite of the planet Saturn, is unique among the icy satellites in its possession of a dense atmosphere. Like the Earth, the dominant atmospheric gas is nitrogen, but the interesting optical effects are controlled by the trace gases. After nitrogen, the most abundant gases are methane (≤4%) and hydrogen (∼0.4%, Waite et al., 2005). Argon was thought to be present at the few percent level, but recent measurements by the INMS measurement on the Cassini spacecraft indicate much smaller mixing ratios (∼10⁻⁶). Solar UV penetrating into Titan’s mesosphere breaks methane down into CH₃ radicals which combine at lower altitudes to form higher order hydrocarbons (such as C₂H₆ and C₃H₈). N₂ is also broken down (by cosmic rays and electrons from Saturn’s magnetosphere) and combines with other molecules to form various nitriles.

Titan’s most visible feature is the optically thick haze layer enveloping the planet about 200 km above the surface. The exact composition of the haze particles is unknown, but spectra of laboratory produced compounds known as Titan tholin provide a good fit to the Voyager observations. These tholin are composed of carbon, nitrogen, and hydrogen molecules in various abundances but typical ratios are of order C/H ≈ 1, C/N ≈ 5

∗ Corresponding author. Fax: +1 303 546 9687.
E-mail address: ebarth@boulder.swri.edu (E.L. Barth).
Titan’s methane–ethane clouds

Cassini and ongoing ground-based observations have both given us more information on the frequency and duration of these clouds and found evidence for clouds at mid-latitudes. Roe et al. (2005) reported the first evidence for mid-latitude clouds, located near 40° S. Their altitudes are confined to the troposphere and spatial extents range from several hundred to several thousand kilometers. Porco et al. (2005) report on observations made by the Imaging Science Subsystem (ISS) on board the Cassini orbiter. They imaged the south polar and mid-latitude clouds and describe a third class of clouds consisting of large-scale nearly zonal streaks (at latitudes of 36–39° S and 67–72° S).

The clouds described above are not the direct focus of this paper (though we apply this model to the formation of the southern polar clouds in [Barth and Toon, 2004]). Our goal in this paper is to understand clouds which are supported by the mean circulation as represented by an eddy diffusion coefficient. The growth rate [given below, Eq. (3)] is determined by the supersaturation \( S = p_a/p_{vap} \), the ratio of partial pressure to saturation vapor pressure. In the steady state, \( S \) is driven by mean motions controlling the value of \( p_a \). In reality, most condensational clouds are controlled by \( p_{vap} \) as atmospheric motions alter atmospheric temperatures which in turn influence \( p_{vap} \) exponentially. We discuss such dynamically driven clouds in [Barth and Toon, 2004]. In the mean however, cloud properties must be in mass balance with the vapor supply. It is that mass balance we hope to elucidate here.

In addition to the cirrus-like clouds described by Bouchez (2004), our model (in its present form, though with different volatiles) is also suited to describe the stratospheric phenomenon described by Coustenis et al. (2001). They used adaptive optics to take the first images of Titan in the J band. The morning side of Titan is brighter than the evening limb by about 9% (J1), 16% (J2) and less than 5% (H1 and H2). The low phase angle of the Coustenis et al. (2001) observations would cause an evening limb brightening, eliminating phase effects as the cause of this feature. The altitudes probed by the J2 filter constrain this feature to be between 70 and 100 km. In images taken by Roe et al. (2002) a similar increase in morning limb brightness was seen. But in this case the morning limb corresponded with the solar angle and it is not possible to rule out phase effects as the cause of the brightening. Recent Keck AO observations reported by de Pater et al. (2005), however, also support the possibility of morning condensation in Titan’s stratosphere.

In this study, we will address the following questions:

1. What are the steady state altitude, size and optical depth of methane clouds?
2. Will a significant fraction of the particles remain ethane?
3. Can any methane clouds be sustained without a surface source of methane vapor?
4. Can an ethane haze be sustained above the tropopause with methane clouds in the troposphere?
5. How does nitrogen dissolved in methane affect cloud formation?
6. What controls the mean methane precipitation rate?
In (Barth and Toon, 2003) we followed the microphysics of steady state ethane clouds in Titan’s atmosphere. Here we continue our studies of Titan’s clouds by adding methane to the model. Section 2 describes the changes to the microphysics model to allow multiple gases to nucleate onto the clouds. Model simulation results and a discussion of the questions listed above are given in Sections 3–6. Additional laboratory measurements that would aid in the understanding of Titan’s clouds as well as model applications with regard to clouds observed in Titan’s atmosphere are outlined in Sections 7 and 8. We conclude in Section 9.

2. Changes to the microphysics model to include methane

Methane properties used in the base model are listed in Table 1. In the base model, methane is allowed to nucleate only onto ethane coated tholin particles [where ethane nucleation follows that described in (Barth and Toon, 2003)]. The Lellouch and Hunten (1987) methane profile is used (Fig. 1), uniformly increased so that the maximum humidity is 98% (consistent with our initialization for ethane humidity). Since methane is destroyed photochemically in the upper atmosphere, there is no downward flux of methane across the top boundary of the model [though, since ethane is a product of methane destruction, there is a flux of ethane into the top of the model as described in (Barth and Toon, 2003)]. At the surface, there is loss through the precipitation of cloud particles but no flux of volatiles into the model to account for surface sources (except for special cases described in Section 3.2).

The condensation (or sublimation) of a vapor onto a cloud particle releases latent heat resulting in a temperature gradient between the droplet surface and its environment. Conduction of heat away from the droplet balances this latent heat release:

\[ 4\pi r f_j c_p (T_i - T_f) = \sum_i -L_{\text{evap},i} \frac{dm_i}{dr}, \]

where \( r \) is the droplet radius, \( f_j \) is the mean ventilation coefficient for heat transfer, \( c_p \) is the thermal conductivity of air (corrected for non-continuum effects), \( T_i \) is the temperature of the environment and \( T_f \) is the droplet temperature. \(-L_{\text{evap},i}\) is the latent heat of condensation (or fusion for ice crystals as we use for most of our cloud models) and \( dm_i/dr \) is the growth rate for each condensing species \( i \). From mass balance,

\[ \frac{dm_i}{dr} = 4\pi r^2 \rho \frac{dr}{dr}, \]

where \( \rho \) is the droplet density. Finding an expression for the growth rate of a condensing species involves combining Eqs. (1) and (2) to eliminate \( T_f \) and introducing the saturation ratio (\( S \)) through the ideal gas equation and the Clausius–Clapeyron equation. The growth rate for species \( i \) in a multi-component particle is related to other components by

\[ \frac{dm_i}{dr} = \alpha_i \left[ \beta_i - \gamma_i \sum_{j=1,j\neq i}^n L_j \frac{dm_j}{dr} \right]. \]

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formulaa</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane vapor properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial distribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor pressure(^b) (ice)</td>
<td>log(_{10}(P) = 4.425070 - 453.92414/T - 4055.6016/T^2 + 115352.19/T^3 - 1165560.7/T^4 )</td>
<td>Lellouch and Hunten (1987)</td>
</tr>
<tr>
<td>Vapor pressure(^b) (liq.)</td>
<td>log(_{10}(P) = 3.901408 - 437.54809/T + 1598.8512/T^2 - 154567.02/T^3 )</td>
<td>Moses et al. (1992)</td>
</tr>
<tr>
<td>Nucleation and growth properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density of methane</td>
<td>0.4228 g/cm(^3) (liq.), 0.519 g/cm(^3) (ice)</td>
<td>Lorenz (1993)</td>
</tr>
<tr>
<td>Diffusivity of methane in N(_2)</td>
<td>D = 0.196 ( \frac{\rho}{\sqrt{RT}} ) (^{1.75} )</td>
<td>From vapor pressure equation</td>
</tr>
<tr>
<td>Latent heat of methane liq.</td>
<td>( L_T = \frac{6}{53}[437.54809 - 3197.7024/T + 463701.06/T^2] \ln 10 )</td>
<td>From vapor pressure equation</td>
</tr>
<tr>
<td>Latent heat of methane ice</td>
<td>( L_T = \frac{6}{53}[453.92414 + 8111.2032/T - 346056.57/T^2 + 466224.28/T^3] \ln 10 )</td>
<td>From vapor pressure equation</td>
</tr>
<tr>
<td>Surface free energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_4) liquid–air</td>
<td>( \sigma_{lv} = 16.33 \left( \frac{180.7 - T}{395.8 - T} \right) )^(0.9)</td>
<td>Yaws (1992)</td>
</tr>
<tr>
<td>CH(_4) ice–air</td>
<td>( \sigma_{lv} = \left( \frac{L_{\text{evap}}}{4u_{LV}} \right)^2 \sigma_{lv} )</td>
<td>Guez et al. (1997)</td>
</tr>
<tr>
<td>CH(_4) ice–CH(_4) liquid</td>
<td>( \sigma_{ld} = \sigma_{sv} - \sigma_{lv} )</td>
<td></td>
</tr>
<tr>
<td>Critical saturation, contact parameter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_4) nucl onto C(_2)H(_6)</td>
<td>( S_{\text{crit}} = 1.1, m = 0.981 )</td>
<td>Curtis et al. (2003)</td>
</tr>
<tr>
<td>CH(_4) nucl onto tholin</td>
<td>( S_{\text{crit}} = 1.1, m = 0.981 )</td>
<td>Curtis (personal communication)</td>
</tr>
<tr>
<td>C(_2)H(_6) nucl onto tholin</td>
<td>( S_{\text{crit}} = 1.15, m = 0.986 )</td>
<td>Curtis (personal communication)</td>
</tr>
</tbody>
</table>

\(^a\) The equivalent equations for ethane as well as atmospheric parameters are given in (Barth and Toon, 2003).
\(^b\) All units are cgs unless otherwise noted.
\(^c\) Also nucleation at \( S_{\text{crit}} = 1.0 \).
\(^d\) Also nucleation at \( S_{\text{crit}} = 1.40 \).
where

\[
\alpha = \frac{4\pi r D'_v f_v M p_{\text{vap}}^i}{RT} \left[ 1 + \frac{D'_v f_v L^2 M^2 p_{\text{vap}}^i}{R^2 T^3 f_i k'_a} \right]^{-1},
\]

\[
\beta = S - AKAs,
\]

\[
\gamma = \frac{LM}{f_i k'_a RT^2} 4\pi r AKAs,
\]

\[
AKAs = \exp \left( \frac{2M\sigma}{RT \rho r} - \frac{3n_s M}{4\pi \rho (r^3 - r_s^3)} \right),
\]

and \(D'_v\) is the diffusivity of species \(i\) (corrected for non-continuum effects), \(f_v\) is mean ventilation coefficient for vapor diffusion, \(M\) is the molecular weight of the species \(i\), \(p_{\text{vap}}^i\) is the saturation vapor pressure for species \(i\), \(R\) is the universal gas constant and \(T = T_\infty\). The ventilation terms \((f_v\) and \(f_i\)) are described in greater detail in (Barth and Toon, 2003).

The correction to the diffusivity is \(D'_v = D_v/(1 + \lambda Kn)\), where

\[
\lambda = \frac{1.33Kn+0.71}{Kn+1} + \frac{4(1-n_s^2)}{9n_s},
\]

\(Kn\) is the Knudsen number and \(\sigma_g\) is the sticking coefficient for growth (or mass accommodation coefficient) and is set to 0.93 for ice. A similar equation follows for the correction to the thermal conductivity, where the Knudsen number is a function of the thermal free path and \(\sigma_g\) is replaced by the thermal accommodation coefficient (set to unity). The parameters in the Kelvin and solute effects term \((AKAs)\) are surface tension \(\sigma\), moles of solute \(n_s\), and radius of insoluble material \(r_s\). Note that for a single condensing species, Eq. (3) reduces to \(\alpha\beta\) and is equivalent to Eq. (8) in (Barth and Toon, 2003). The \(\gamma\) correction term for multicomponent growth is generally small.

Nucleation of methane removes an ethane cloud particle, creating a methane ice crystal with both an ethane and a tholin core. This mixed cloud particle can condense additional methane and/or ethane depending on environmental conditions. For our methane and ethane ice particles we ignore the solute effect (see later discussion for nitrogen dissolved in liquid methane droplets). Depending on the sign of \(dm/dt\), methane and ethane condense and evaporate independently, or together at a ratio of \(dm/dt_i/dm/dt_{tot}\). When the methane shell has completely evaporated, the particle returns to an ethane ice crystal with a tholin core. Further total evaporation returns a tholin particle. The tholin core is released as a size distribution; the ethane clouds are returned to a monodisperse distribution at their average size.

### 3. Steady-state model results and sensitivity tests

In this section we describe a series of models designed to understand the mean behavior of Titan’s clouds and the sensitivity to various model parameters which are poorly constrained by our current knowledge of Titan. We start by describing the results from our base model which uses the parameters given in Table 1. We then give the results from models which alter one parameter from its default value in the base model. First we change some parameters from our simulated Titan atmosphere by exploring the role of surface sources of methane and ethane (Section 3.2) and increasing the eddy diffusion by a constant factor (Section 3.3). Next we explore parameters relevant to the nucleability of methane clouds such as the phase of the methane in the cloud (Section 3.4), the number and size of the tholin CCN (Section 3.5), and the critical saturation for the clouds (Section 3.6).

A comparison of the results from the sensitivity tests is given in Table 2. The table lists the altitudes of the ethane and mixed clouds, the total cloud optical depth and the maximum saturation methane can attain after the initialization of cloud formation. Each case is described with greater detail below. Each subsection begins with the motivation behind the sensitivity test and a description of the model parameters which differ from those in the base model.
Clouds have a broad size distribution between 10 and several microns, but with smaller increases in optical depth (Fig. 9). Sensitivity tests

### Table 2

<table>
<thead>
<tr>
<th>Model description</th>
<th>Ethane clouds</th>
<th>Mixed clouds</th>
<th>Optical depth</th>
<th>Max $S$ for CH$_4$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base model</td>
<td>0–10 km, 30–40 km</td>
<td>0–30 km</td>
<td>0.15</td>
<td>1.06</td>
<td>Only affects mass of clouds in lower 10 km; rains out more ethane near surface</td>
</tr>
<tr>
<td>Surface source of methane</td>
<td>0–5 km, 30–40 km</td>
<td>0–30 km</td>
<td>0.18</td>
<td>1.06</td>
<td>Additional ethane clouds below 10 km; no effect on mixed clouds since methane subsaturated here</td>
</tr>
<tr>
<td>Surface source of ethane</td>
<td>0–10 km, 30–40 km</td>
<td>0–30 km</td>
<td>0.20</td>
<td>1.06</td>
<td>Eddy diffusion increased** 0–10 km, 30–40 km 3.00 1.07 Periodic cloud formation with short-lived high $r$ clouds but little change in $S$</td>
</tr>
<tr>
<td>Ice and liquid methane clouds</td>
<td>0–20 km, 30–40 km</td>
<td>0–15 km (a) 15–30 km (b)</td>
<td>0.20</td>
<td>1.08(a) 1.06(b)</td>
<td>Most liquid mixed clouds formed through melting leaving a larger number of ethane clouds in bottom 20 km</td>
</tr>
<tr>
<td>Initial tholin decreased</td>
<td>0–10 km, 30–40 km</td>
<td>0–30 km</td>
<td>0.1–0.17</td>
<td>1.09</td>
<td>Initial #ccn decreased 0–10 km, 0–30 km 0.20 1.06 Reaches methane $S &gt; 1.5$ for $10^7 \times$ less tholin particles, but $&gt;1000 \times$ less cloud particles</td>
</tr>
<tr>
<td>Larger CCN for ethane</td>
<td>0–10 km, 30–40 km</td>
<td>0–30 km</td>
<td>0.20</td>
<td>1.06</td>
<td>Ethane cloud particles 10$\times$ larger, but still smaller than 100 µm</td>
</tr>
<tr>
<td>Higher $S_{crit}$ for ethane</td>
<td>0–10 km, 35–40 km</td>
<td>0–35 km</td>
<td>0.09</td>
<td>1.10</td>
<td>Higher #ccn 0–10 km, 35–40 km 0–35 km</td>
</tr>
<tr>
<td>CH$<em>4$ clouds $S</em>{crit} = 1.1$</td>
<td>0–5 km 10–40 km</td>
<td>0–35 km (c) 0–30 km (d)</td>
<td>0.32</td>
<td>1.04</td>
<td>Similar number of mixed cloud particles but addition of pure methane clouds doubles the optical depth</td>
</tr>
<tr>
<td>No ethane clouds $S_{crit} = 1.1$</td>
<td>0–25 km (methane only)</td>
<td>0–25 km (methane only)</td>
<td>0.32</td>
<td>1.04</td>
<td>Number of methane cloud particles similar to mixed clouds in CH$<em>4$, $S</em>{crit} = 1.1$ case</td>
</tr>
<tr>
<td>CH$<em>4$ clouds $S</em>{crit} = 1.0$</td>
<td>0–40 km</td>
<td>5–35 km (c) 0–35 km (d)</td>
<td>0.48***</td>
<td>1.005</td>
<td>Periodic cloud formation (all cloud types) with short-lived high $r$ but no methane supersaturations</td>
</tr>
</tbody>
</table>

* Geometric limit.
** Numbers listed refer to the $10 \times K_{diff}$ case. Other cases where the eddy diffusion coefficient was increased by factors of 2 and 5 showed similar periodic clouds but with smaller increases in optical depth (Fig. 9).
*** Median value.

(a) Liquid, (b) ice, (c) mixed methane–ethane, (d) pure methane.

#### 3.1. Results from base model

In our base model, both ethane clouds and mixed (methane–ethane) clouds form (Figs. 2 and 3). Our ethane cloud model described in (Barth and Toon, 2003) produced steady state ethane clouds between 8 and 58 km in Titan’s atmosphere. However, Fig. 2 shows that ethane clouds only remain between 30 and 40 km, and 0–10 km when methane is allowed to condense. Mixed clouds dominate by mass from the surface to 35 km.

The size distribution of the ethane clouds has a peak radius around 10 µm. The mixed cloud particles are much larger, indeed they are precipitation sized particles formed by condensation. The small amount of ethane limits cloud particle nucleation, leaving most of the tholin particles untouched. The scarcity of ethane cloud particles limits the number of condensation nuclei for the methane, however the rapid growth times for methane on the mixed clouds reduces methane vapor in the troposphere to only modest supersaturations ($\sim 105\%$ near 30 km). The mixed cloud particles are most abundant by number between 5 and 30 km but have very small concentrations ($\sim 5 \times 10^{-5} \text{ cm}^{-3}$). At 30 km clouds have a broad size distribution between 10 and several 100 µm, with the smaller particles being more than 50% ethane and the largest particles having almost no ethane. For comparison a typical cirrus cloud on Earth would have 10 to $10^5$ times as many particles/cm$^3$ with particle sizes between 10 and 100 µm. The cloud particles near the surface have grown to millimeter sizes. Most of the ethane cloud particles ($\sim 10^{-3} \text{ cm}^{-3}$) remain between 30 and 40 km. Methane nucleation removes all of the pure ethane clouds at altitudes above about 10 km. At 10 km, both methane and ethane are subsaturated. Another layer of ethane clouds remains near the surface with abundances about 10 times less than those at the tropopause.

Our model is not fully at steady state even though this run extended for 800 terrestrial years because methane and ethane can rain out providing a sink, but there are no compensating sources for methane. (However, ethane has reached a steady state balance between the rainout of ethane in cloud particles and vapor resupply at the top of the model. This happens after about 700 years.) Fig. 4 shows the total mass of methane and ethane in the atmosphere. These decline from their initial values and then begin to level out as precipitation declines.

The methane column abundance decreases slowly with time; the initial value is 335.9 g/cm$^2$. It is 297.2 g/cm$^2$ at 650 years,
Titan’s methane–ethane clouds

Fig. 2. Number density and mass mixing ratio profiles for the ethane (dashed) and mixed clouds (solid) in the base model after a simulation time of approximately 800 (terrestrial) years.

Fig. 3. Size distribution of cloud particles in the base model for various altitudes. The two leftmost plots are size distributions for pure ethane clouds and mixed methane–ethane clouds, respectively. The rightmost plot shows the ethane mass fraction of the mixed clouds. The legend shown in the last plot applies to all three.

Fig. 4. Total mass of methane and ethane (vapor plus condensed) in the base model as a function of time (solid line). Also shown are models with a surface source of methane (dashed lines) and a surface source of ethane (dotted line). The initial amounts are $1.68 \times 10^{-3}$ g/cm$^3$ for methane and $2.35 \times 10^{-7}$ g/cm$^3$ for ethane.

Over the course of the model simulation the average loss of methane is $\sim 12\%$ in 800 years, and the loss of ethane is $\sim 80\%$. The fraction of tholin lost to nucleation is about $1$ in $10^6$. Despite these losses the model is tending to a steady state with the time to partially mix the entire 100 km column with an eddy diffusion coefficient of $K_{\text{diff}} = 5000$ cm$^2$/s. At $\sim 100$ years (the time to partially mix the troposphere) the column abundance of methane (for the 100 km of the model) is $318$ g/cm$^2$.

Fig. 5. Methane mixing ratio which results when methane clouds form on ethane coated tholin particles for no surface methane source (base model), shown at a simulation time of $\sim 800$ years.
zero precipitation rate such that even without surface sources, clouds could form in the atmosphere.

The methane mixing ratio (Fig. 5) is approximately constant down to 20 km (at $1.4 \times 10^4$ ppm) and increases to $4 \times 10^4$ ppm at the surface due to the supply of methane from evaporating cloud particles.

3.2. Methane resupply

The methane in Titan’s atmosphere is constantly being broken down due to bombardment by solar ultraviolet light in the upper stratosphere. If the current photolysis rate has been constant with time, then the current budget of methane would be destroyed in less than 50 million years. So, either Titan has been depleting its atmospheric methane over the age of the Solar System, or, as is widely believed, there is a source of methane resupply at Titan’s surface. If nothing else, the falling precipitation may be recycled.

Fig. 4 compares the amount of methane remaining in the steady-state model when a surface source is added to that of the no source (base) model. We chose to model a surface methane source by maintaining a minimum methane humidity in the bottom model layer. This value was set by the surface methane abundance from (Lellouch and Hunten, 1987) and is equivalent to a relative humidity to ice ($RH_i$) of 50%. Recent work by Lemmon et al. (2002) points to a slightly lower surface humidity of $RH_i = 30\%$. (The value quoted in their paper of 32% refers to the liquid case, $RH_l$; at Titan’s surface the saturation vapor pressure of methane with respect to liquid is around 90% that of methane with respect to ice.) They also note that supersaturation in the stratosphere results in a slightly smaller surface methane mole fraction equivalent to a relative humidity of $RH_i = 25–27\%$. These measurements apply to equatorial regions and do not include seasonal changes (the measurements were taken in 1997, northern fall). Our no source model described in Section 3.1, maintains a bottom layer humidity around $RH_i = 40\%$, so the Lemmon et al. (2002) data are consistent with there being no active resupply at the surface.

Above 10 km, the ethane and mixed cloud results are similar to those of the base model (Figs. 2 and 3). The additional methane from the surface results in more millimeter-sized mixed cloud particles (which are almost pure methane with only a small ethane core) near the surface. The average rainout rate of these precipitation particles is $\sim 0.2$ cm/(terrestrial) year. This value is comparable to the 0.6 cm/year calculated by Lorenz (2000) based on the amount of energy available for convection. Without the surface source, the rainout rate (averaged over 800 years) is a factor of 10 smaller, and tends toward zero. The higher methane humidity in the surface source model means fewer pure ethane cloud particles are present near the surface.

Ethane is probably the dominant liquid in lakes, in order to explain the expected low methane surface humidity. (Titan’s surface temperature is above the melting point of ethane.) We simulate the effects of ethane (but not methane) resupply at the surface by fixing the bottom layer (ethane) humidity to 75%. The additional ethane results in about 10 times more mass of ethane clouds below 10 km due to more cloud particles and larger radii. The size distribution peaks at about 20 µm and the number of particles is $10^6$ times more abundant than in the base model. The mixed clouds above 10 km are unaffected, and the mass of mixed clouds at the surface is only slightly greater due to larger particles. Overall ethane mass is increased by $\sim 75\%$, whereas methane loss is the same as in the base model. The methane surface humidity is not fixed, but remains near 45%. If more methane was present due to a surface source, the results are similar to both of the above described surface source models—large mixed cloud particles are found near the surface (raining out at an increased rate), but a substantial ethane cloud particle layer still remains at 10 km. Fig. 6 illustrates how each surface source model affects the number and mass of cloud particles compared to the no surface source (base) model. In all

![Fig. 6. Influence of a surface source on the number and mass of cloud particles. The lines show the change (i.e., increase/decrease by a factor of $\times$) in cloud number density (left) and cloud mass density (right) referenced to the base model results for the three surface source cases studied: surface methane source (dash), surface ethane source (dot) and surface sources of both (solid).]
cases, cloud formation prevents the additional methane and/or ethane supplied at the surface from influencing the evolution of the atmosphere above an altitude of about 10 km.

3.3. Changes to eddy diffusion

Barth and Toon (2003) discusses the uncertainty in the eddy diffusion profile we use in our model. Here (Figs. 7 and 8) we explore a case where we increased the eddy diffusion coefficient ($K_{\text{diff}}$) by a factor of 10 (the nominal value of $K_{\text{diff}}$ is 5000 cm$^2$/s up to 90 km). Increasing $K_{\text{diff}}$ results in a swifter resupply of vapor to the altitudes where clouds have removed the vapor. As with our ethane clouds in (Barth and Toon, 2003), a periodicity becomes evident when $K_{\text{diff}}$ is increased. We see significant optical depths which last a few terrestrial days. Fig. 9 shows how the peak cloud optical depth becomes greater as the eddy diffusion factor is increased. The period of the cycle is around 11 terrestrial days and does not vary significantly between the eddy diffusion factor cases. Fig. 10 shows that this cloud formation is followed by small fluctuations in $S$. In the base model, these fluctuations are only minor and so the optical depth increases were not discernible. The formation and evaporation of the mixed clouds is significant enough to cause an oscillation in the total methane column mass. Fig. 8 indicates that the increases in optical depth are mainly due to an increase in the number of cloud particles rather than a change in the size distribution; comparison of the top two plots shows only slightly smaller particles at the optical depth minimum (day 8), but significantly more particles at the optical depth maximum (day 9). This periodicity in cloud formation is the same phenomenon we saw with our ethane clouds [described in (Barth and Toon, 2003)]. It results from the competition between nucleation and growth depleting the ethane vapor content of an atmospheric layer and transport resupplying the vapor. In our previous modeling with only ethane clouds, we confirmed that the period of oscillation was a numerical artifact through simulations with a finer altitude-grid resolution, so we do not repeat such a test here. Fig. 11 shows the optical depth of the ethane cloud layer at 40 km. The same timescale for the peaks in cloud optical depth is evident between the pure ethane clouds and the mixed clouds (Fig. 9). As the ethane clouds provide the only CCN for the mixed clouds in these simulations, we are seeing how the optical depth of methane clouds is controlled by the number of ethane particles in the atmosphere. While the periodicity may be an artifact of the 1D model, on Titan cloud formation could quickly deplete methane and time will be required for it to be resupplied by dynamics. However, we do not expect periodic behavior on Titan, but rather episodic cloud formation.

3.4. Clouds composed of liquid droplets

Nitrogen dissolved in methane lowers the freezing point and depresses the vapor pressure. In Titan’s troposphere the temperature drops below 80 K, the freezing point of methane with 10–20% nitrogen, above about 15 km. When methane ice falls to 16 km, we initiate melting with a constant loss rate of 100 s$^{-1}$ (the default model value).

Fig. 12 compares the vapor pressure of frozen methane, pure liquid methane, and liquid methane doped with nitrogen. We simulate the addition of dissolved nitrogen in the (liquid) methane clouds by depressing the saturation vapor pressure by a set amount, found in (Thompson et al., 1992). They used a thermodynamic model for vapor–liquid equilibrium in the N$_2$ + CH$_4$ system to evaluate the saturation criteria, composition of condensate, and latent heat for a nominal Titan pressure–temperature profile. They found that nitrogen comprises about 16–30% of the volatile content of the cloud particle, with the nitrogen enrichment increasing with altitude. We use their saturation mole fractions as an adjustment factor to the (pure) liquid methane saturation vapor pressure equation in our model. This adjustment factor varies with altitude (since the nitrogen content varies) but, in general, results in about a 20% decrease in the liquid vapor pressure of pure methane.
Fig. 8. Size distribution of cloud particles in the model where the eddy diffusion coefficient has been increased by a factor of 10. The clouds are shown at an altitude of 26 km at four times in the cycle corresponding to minimum optical depth, first peak in optical depth, second peak in optical depth and at about 1/3 of the peak optical depth.

Fig. 9. Optical depth with time for models where the eddy diffusion coefficient was increased by a factor of 2 (dash), 5 (dot), and 10 (dash-dot). The solid line shows the optical depth for a model with our nominal $K_{\text{diff}}$ value.

Fig. 10. Changes in methane saturation, $S$, with time for models where the eddy diffusion coefficient was increased by a factor of 2 (dash), 5 (dot), and 10 (dash-dot). The solid line shows $S$ for the model with our nominal $K_{\text{diff}}$ value.
The number density and mass profiles of the clouds are shown in Fig. 13. Nucleation of liquid methane occurs initially near 16 km, but does not continue throughout the course of the model run. The liquid clouds present at the end of the simulation (Fig. 13) are there due to the melting of falling ice crystals. Fig. 14 shows similar particle sizes to those in Fig. 3 for the mixed clouds. We do not see the 9 mm raindrops described by Lorenz (1993) perhaps because the small number of cloud particles makes coalescence inefficient. We do, however, have some methane droplets reaching the surface, whereas Lorenz (1993) (e.g., Fig. 4) found that methane raindrops would totally evaporate in the atmosphere. In our 2 km layer, the droplet diameters are between 0.01 and 2 mm. The fall velocity for a 1 mm diameter raindrop is about 10% higher in our model than in Lorenz, most likely due to the differences in the density of the droplets (we include the density of the solid ethane core, 713 kg/m$^3$, whereas Lorenz (1993) uses a density of 600 kg/m$^3$). Also, our evaporation rates are slower as we are including the effects of dissolved N$_2$ and include additional terms in the growth equation [see Barth and Toon, 2003, Eq. (8)].

Samuelson and Mayo (1997) also modeled the formation of methane cloud particles around ethane cores. In their steady-state model the supply of ethane is fixed by the Yung et al. (1984) results (as in our model). They do not explicitly model the nucleation and growth of the ethane particles but rather look at a number of cases where the ethane particle radius ranges from 10 to 150 µm. The ethane flux then constrains the number of cloud particles that can form, i.e., large particles will be less abundant. Methane begins to grow on the ethane nuclei once these particles fall to the altitude of methane saturation. Growth is described in a manner similar to that in our model, with some simplifications and neglecting any ethane growth. Above about 12 km, methane cloud particles are modeled as octahedral ice crystals and below as liquid droplets composed of a mixture of methane and nitrogen. They, like Lorenz, are able to produce large methane droplets, but methane droplets greater than a few millimeters in radius require the ethane core to be at least 50 µm. In fact, the smallest ethane core they consider (10 µm) is about twice as large as our ethane particles at altitudes near the tropopause where methane nucleation commences (hence our mixed cloud particles at 10 km have an effective radius of about a millimeter, whereas their particles are closer to 2 mm). However, comparing the results of our liquid methane cloud model with their results for the 10 µm ethane core case shows similar methane mole fraction and supersaturation profiles.

Since the saturation vapor pressure of liquid methane is less than that of ice methane, the liquid clouds grow faster but evaporate more slowly than the ice clouds given the same methane concentration. Also, the methane droplets fall more slowly than methane ice crystals due to their lower density. Since nucleation of liquid clouds is not occurring (they are forming through melting) and ethane is supersaturated above 10 km, we see about 100 times more ethane cloud particles near the surface in this model compared to the base model.

### 3.5. Changes to initial tholin

The tholin particles, which we consider the initial condensation nuclei, are small enough to be transported mainly by eddy diffusion. Our initial tholin profile was made by allowing diffusion to transport these particles for 500 years; until the flux of particles to the surface matched the production rate. We explore various scenarios to understand the sensitivity of the clouds to the initial tholin profile. We find that even halving the tholin abundance produces no significant effect on the clouds, as the ethane only nucleates on at most 1% of the tholin at a given altitude.
Fig. 13. Number density and mixing ratio profiles for the ethane (dashed) and mixed clouds (solid) in the model which allows liquid methane clouds to form. Nucleation was found to be inefficient in forming the liquid mixed clouds; those clouds shown are a result of melting. Results are shown at a simulation time of \( \sim 800 \) years. The profiles for the base model clouds are also shown (dotted lines).

Fig. 14. Size distribution of cloud particles in the model which allows liquid methane clouds to form. The ice and liquid mixed clouds are shown on the same plot. Results are shown at a simulation time of \( \sim 800 \) years. The legend in the last plot applies to all three.

The ethane clouds do not begin to affect the tholin profile by more than a few percent (Fig. 15) until the flux of tholins is decreased by a factor of 100. Total loss of tholin where cloud formation is happening does not occur until the initial tholin is decreased by a factor of \( 10^4 \). Since it is not likely that our initial tholin profile is off by such a large factor, it seems unlikely that cloud formation alone can clean the atmosphere of haze particles.

It is possible that the tholin which serve as condensation nuclei for Titan’s ethane clouds are larger than those we use in our model due to nucleation of other hydrocarbons above the altitude where ethane will begin to condense. Cabane and Chassefière (1995) give equatorial mixing ratios of \( 2.2 \times 10^{-6} \) for acetylene and \( 9.0 \times 10^{-8} \) for ethylene. Recent measurements by Roe et al. (2003) indicate a propane abundance of \( 6.2 \times 10^{-7} \) between 90 and 250 km. Each of these minor species will reach their condensation temperatures at altitudes above that of ethane condensation (Sagan and Thompson, 1984). We will use tholin particles coated with these other hydrocarbons as nuclei for both ethane and methane. We simulate these hydrocarbon coated tholins by initiating the larger part of the tholin population using ethane cloud data from our ethane-only cloud model (described in Barth and Toon, 2003). The number of these hydrocarbon coated tholins is uniformly decreased by a factor of 10 (from the number of clouds in the ethane-only cloud model) since acetylene, ethylene, and propane are less abundant than ethane, and hence we would expect fewer cloud particles to form from the condensation of these gases. We also expect a significant portion of the tholin population to remain uncoated by other hydrocarbons [as this was seen for the ethane clouds in (Barth and Toon, 2003)]. Thus the initial tholin distribution for this simulation is bimodal, as shown in Fig. 16.

The saturation vapor pressures of these species are generally less than that of ethane, so we regard the number and size of these particles to be an upper limit. (We ignore any additional condensation of these species as their vapor pressures are much lower than that of ethane near the tropopause.) We insure a continuous supply of these particles by including a flux at the top of the model. This flux was calculated by \( V_{\text{fall},100} \times N_{\text{avg}} \), the fall velocity of ethane cloud particles at 100 km multiplied by the average number of hydrocarbon coated tholin particles in the initial profile. The smaller (bare) tholin are also continuously supplied, by the same flux used in our previous models.
The number density of ethane and methane clouds and mixing ratio profiles for the modified tholin case (Fig. 17) are comparable to the base case. Less than 1% of the tholin particles are nuclei for clouds for both models. One noticeable difference is that there are less ethane cloud particles near the surface in the larger tholin particle simulation—presumably because their faster fall velocities allowed more of these larger ethane particles to reach the surface. This is consistent with the larger precipitation rate found in the larger tholin simulation (a factor of 2 greater than in the base model). The ethane clouds in the top 10 km of the troposphere are 2–5 times more massive than those in the base model. Both the ethane and mixed clouds near the surface are more massive in the large tholin case (up to 15% at the surface), but only up to 10 km (above this altitude any differences are negligible, except as noted above for the ethane clouds).

Fig. 18 shows that larger CCN for the ethane clouds results in the size distribution peaks for the ethane clouds at 10 and 40 km shifting to larger radii—about 20 µm here compared to 5 µm in the base model at 40 km (the 10 km ethane clouds in the base model were not abundant enough to be seen in the size distribution plot). Both models show comparable sizes for the ethane cloud particles at 30 km. The mixed clouds have a broader size distribution at 10 km but still do not grow larger than a couple of millimeters (same maximum size as in the base model).

In their steady state methane condensation model (discussed in the previous section), Samuelson and Mayo (1997) calculated that ethane cloud particles serving as condensation nuclei for methane clouds needed to be at least 100 µm in radius if a methane supersaturation was to be maintained in the presence of methane condensation. Our ethane clouds, even with larger cores, still do not reach sizes of 100 µm and so we do not see huge methane supersaturations (in fact, we see the same methane saturation value as in the base model, 1.06). Ethane and other hydrocarbons grow slowly so it does not seem likely that ethane cloud particles could grow to sufficient sizes such that the methane clouds fall out too rapidly to reduce $S$. Alternatively, one can reduce the number of ethane particles to achieve this same effect as discussed below.

### 3.6. Nucleation of ethane and methane on bare tholin

The low vapor pressures of ethane and other hydrocarbons results in a scenario where cloud particles only grow to a few 10s of microns, thereby limiting the amount of vapor they can remove from the atmosphere. Their humidities remain near their critical saturation. Methane grows much faster and can generally bring the methane content of the atmosphere to near saturation through the growth of cloud particles.

The critical saturation for the nucleation of ethane ice onto tholin has not been measured. Lab measurements of hydrocarbon ice nucleation onto a tholin particle (butane, Curtis et al., 2005) indicate a high critical saturation of 1.4. Ethane may have a comparable critical saturation; we consider our nominal value of 1.15 only a lower limit. For a higher ethane critical saturation we see large ethane supersaturations, but methane supersaturations only a few percent larger than our base model. Figs. 19 and 20 indicate methane cloud particle number and sizes are similar to the results in our base model when few ethane particles form (Figs. 2 and 3).

We find that even raising the critical saturation for ethane does not sustain large methane supersaturations once the mixed...
clouds start to form (Fig. 21). The introduction of temperature perturbations brings the methane humidity above 140% for brief periods (see Barth and Toon, 2004). However, the growth of methane on the mixed clouds is sufficient to carry away much of the excess methane. We found that the only way to reach such high methane humidities in our steady-state model was to form the methane clouds without the ethane core and restrict the critical saturation to large values (e.g., 1.5 as shown in Fig. 21). We describe below why this may not be a realistic scenario.

The scarcity of adequate condensation nuclei for methane clouds could account for their low optical depths in our base model. However, if methane could nucleate onto the bare tholin particles more cloud particles may form. Recent lab measurements of the critical saturation of methane onto tholin indicate
Titan's methane–ethane clouds

Fig. 20. Size distribution of cloud particles in the high ethane $S_{\text{crit}}$ model for various altitudes. The two leftmost plots are size distributions for pure ethane clouds and mixed methane–ethane clouds, respectively. The rightmost plot shows the ethane mass fraction of the mixed clouds. The legend shown in the last plot applies to all three.

Fig. 21. Comparison of methane saturation profiles from models with low ($S_{\text{crit}} = 1.15$, dashed line) and high ($S_{\text{crit}} = 1.4$, solid line) nucleation barriers for ethane clouds. Also shown is the methane saturation for a case where only methane clouds are included in the model (dot) but form at a critical saturation of 1.50. The $S_{\text{crit}} = 1.15$ case is our base model.

that the nucleation energy barrier is lower than has been previously thought (Curtis, 2005, personal communication). Values range between 1.0 and 1.10. For the case of 1.10, there is a comparable energy barrier needed to nucleate methane on both bare tholin and ethane coated tholin particles. Figs. 22 and 23 show the number, mass and size distribution for this case. Although the energy barriers are the same, the ethane coated particles are favored as nuclei due to their larger size. Additionally more pure ethane clouds can remain throughout the troposphere, since there is less methane available to turn them into mixed clouds (note the appearance of ethane clouds at 20 km). The precipitation rate of the pure methane clouds (0.005 cm/year) is half that of the mixed clouds; adding them together gives a rate comparable to that of the mixed clouds in the base model. The optical depth of these clouds is more than twice that of the clouds in the base model (with about 2/3 of the contribution coming from the mixed clouds and 1/3 from the pure methane clouds).

We can also learn more about the clouds described in the previous case ($S_{\text{crit}}$ for methane nucleation onto bare tholin is 1.1) by looking at a case which does not allow ethane clouds

Fig. 22. Number density and mass mixing ratio profiles for all cloud types in a model which allows methane nucleation onto both ethane-coated and bare tholin for a critical saturation of 1.10. The number of mixed cloud particles is about five times higher than in the base model; the mass of mixed cloud particles is nearly identical to the base model clouds.
Fig. 23. Size distribution of methane cloud particles in a model which allows methane nucleation onto both ethane-coated and bare tholin for a critical saturation of 1.10. The fraction (by mass) of ethane in the mixed clouds is less than 0.5% for all sizes and altitudes shown.

Fig. 24. Number density and mass mixing ratio profiles in a model with only methane clouds (which nucleate at a critical saturation of 1.10).

Fig. 25. Size distribution of methane cloud particles in a model which does not include ethane clouds. Methane nucleates at a critical saturation of 1.10. Figs. 24 and 25 show that the number, mixing ratio and size distribution of these pure methane clouds resembles the mixed clouds in the previous case. Optical depth in both cases is the same which shows that (1) ethane clouds do not contribute to the optical depth and (2) methane forms the same number of clouds with or without the ethane coated tholin to serve as nuclei.

A case where it becomes easier for methane nucleation on bare tholin ($S_{\text{crit}} = 1.0$) rather than around ethane coated tholin nuclei ($S_{\text{crit}} = 1.1$) is shown in Figs. 26 and 27. Here the number of mixed cloud particles is drastically reduced and so the ethane clouds no longer form two separate layers, but exist throughout the troposphere. Again comparing the size distributions, it is also interesting to note that the methane and mixed cloud particles here are half the size of those described in the previous, $S_{\text{crit}} = 1.10$ case (and hence a factor of 4 smaller than in the base model). We also see in this simulation a phenomenon similar to that described in Section 3.3 (eddy diffusion sensitivity tests), namely that high optical depth clouds appear and then disappear on short timescales in a roughly periodic manner (Fig. 28). This is because the energy barrier to nucleation has been lowered to the extent that cloud formation exhausts the methane supply faster than it can be resupplied by eddy diffusion.
4. Methane precipitation

If a situation could be reached where methane saturations could build up to a level high enough to allow a large number of these pure methane cloud particles to form (e.g., if there is a lack of suitable nuclei for some period of time or $S$ is suddenly ramped up by a change in temperature), they are able to grow to precipitation size and rain out in less than half a day (Fig. 29). This time is several hours longer than indicated by the observations of Griffith and Hall (2000), but shorter than the lifetimes of the polar clouds observed by Brown et al. (2002). In our steady-state modeling, due to the slow resupply of methane vapor as the only mechanism for increasing the methane saturation, we do not see long lived optically thick clouds. However, we discuss a mechanism to form optically thick clouds with longer lifetimes in (Barth and Toon, 2004). Essentially relatively long-lived clouds can form due to dynamically driven temperature changes, but only over small fractions of the planet’s surface. We do, however, see some precipitation, which is promising in light of the Huygens probe detection of methane in Titan’s surface.
5. Atmospheric methane flux balance

An important issue regarding Titan’s clouds is their average optical depth, or rarity. In the simulations presented here we maintain a steady vapor supply but may produce episodic clouds. Nonetheless a basic principle holds; over any long period of time the cloud sedimentation flux must be in balance with the dynamically driven vapor supply. In steady vapor supply the clouds adjust their mass to achieve balance. The steady state clouds have low mass (Fig. 3) and consequently low optical depth. Clouds produced episodically can have larger optical depths [as discussed in (Barth and Toon, 2004)], but they are present over only short periods of time to limit the downward mass flux. Fig. 30 shows the upward vapor flux and downward sedimentation fluxes for the no source and source cases discussed in Sections 3.1 and 3.2 after reaching mass balance (the no source case should eventually reach zero at the surface). Note that a surface methane source is only influential up to an altitude of 15 km.

Clouds essentially have two ways to adjust—by changing their frequency, or by changing their properties. Here we only allow for property changes, although the high diffusion cases (discussed in Section 3.3) produced oscillations. The properties of note in the mass flux are essentially cloud particle number density and cloud particle radius. The sedimentation flux is \( \frac{N_b t^4}{3\pi r_b^5} V_{\text{fall}} \). However, \( V_{\text{fall}} \propto r^2 \) so sedimentation flux \( \propto N_b t^2 r_b^3 \). \( N_b \) is the number density and \( r_b \) is the particle radius at the cloud base and the cloud base is defined as the altitude where \( S = 1 \). In this equation, \( S \) is fixed by dynamics and \( N \) is controlled by nucleation. However, the flux is adjusted by small changes in \( r \).

We see clouds in the Earth’s atmosphere because the condensation rate of water is fast compared to the fall time of the individual cloud particles. Similarly, we are able to keep clouds in our model due to the fast growth time of methane onto the mixed cloud particles. The saturation vapor pressure of methane at 30 km is about 6.5 mbar. At a saturation of 1, 8.4 \( \times 10^{-6} \) g/cm\(^3\) of methane must be removed to reduce the layer to a saturation of 1. The mass of a cloud particle of radius 10, 50, 100, and 1000 µm (neglecting the tholin core), is 2.6 \( \times 10^{-9} \), 3.4 \( \times 10^{-7} \), 2.7 \( \times 10^{-6} \), and 2.8 \( \times 10^{-3} \) g, respectively. To condense all of this excess methane onto a number of cloud particles of the same size would require 0.003 particles/cm\(^3\) of 1000 µm, 3 particles/cm\(^3\) of 100 µm particles, 30 particles/cm\(^3\) of 50 µm particles, or greater than 3000 particles/cm\(^3\) for 10 µm particles. We initialize the model with 60 tholin particles/cm\(^3\) (total of all sizes) at this altitude. Fig. 31 shows how long it takes to grow methane and ethane on a cloud particle to each of these sizes starting from a 0.1 µm particle (where 0.1 µm is the size of most tholin particles, the growth time is nearly independent of the initial size). For comparison, Fig. 31 also shows the time for these sized particles to fall from 30 to 10 km. Clearly for our steady state clouds there is enough time to grow 1000 µm sized particles before they are removed from the atmosphere, and therefore there is enough time to bring \( S \) to unity.

6. Optical depths of steady state clouds

Fig. 32 shows the cloud optical depths found from the various model runs. The base model and the methane surface source model have nearly identical optical depths, which are negligible. The high ethane \( S_{\text{crit}} \) case has clouds with an optical depth about 100 times higher than the base and surface source models, but still small compared to the tholin. Only with an increase in the number of cloud particles as a result of allowing methane to nucleate on the tholin do the clouds begin to approach the optical depth of the tholin.

The sedimentation flux can be written as \( F_{\text{sed}} = c t r^2 \), where \( t \) is the extinction per km. Since \( F_{\text{sed}} \) is fixed by dynamics, the
extinction is proportional to $F_{sed}/r^3$. To obtain larger $\tau$ one needs smaller particles, as shown in the tholin nucleation section. Alternatively, one can increase $S$ for short periods of time by having clouds form episodically (Barth and Toon, 2004), or one can increase $F_{sed}$ by having a higher eddy diffusion rate.

7. Additional measurements

We can gain a better understanding of Titan’s clouds by further measuring properties of their constituents in the lab. Vapor pressure measurements of Titan’s other hydrocarbons and nitriles at relevant temperatures will help us to understand their incorporation into Titan’s mixed component clouds. A study of the changes to vapor pressure and freezing temperature of ethane when diluted with nitrogen [similar to the study by Thompson et al. (1992) for methane] will be important in determining whether or not ethane clouds can form as liquid droplets. Also, it would be worthwhile to understand if supercooled methane and ethane clouds could form analogous to supercooled water clouds in the terrestrial atmosphere. In
such cases cloud microphysics models will need to be refined to include the mixing of methane and ethane within the cloud droplets.

Most importantly, significant constraints on Titan’s clouds can be found by continuing the measurement of nucleation parameters relevant to Titan cloud formation. Although many minor species other than ethane are also capable of condensing in Titan’s lower stratosphere and troposphere, it may not be necessary to fully understand their contact parameters for nucleation. As we have shown in this study, ethane, although modeled with a relatively small critical saturation, is too vapor limited to produce enough particles to provide optically thick clouds. The only volatile abundant enough to produce the number of particles necessary for visible clouds is methane. An ongoing belief in the Titan community has been the assumption that methane nucleation must be difficult. However, recent measurements (Curtis et al., private communication) have shown methane ice easily forms on tholins. It now becomes important to understand if the liquid methane clouds easily form on tholins. It would also be useful to measure the critical saturation of ethane ice onto tholin.

8. Additional observations and model applications

Clouds on Titan are strongly coupled to dynamics. Producing the mid-latitude and south polar clouds observed in ground-based and Cassini images will required coupling our model to a 3D dynamical model. The microphysical processes described by this model are applicable to all of the clouds which have been seen on Titan. Optimally thick clouds are produced on fast transport timescales driven by dynamics which is not well reproduced in a column model such as described in this paper. Our microphysics model in conjunction with a general circulation model and a regional scale convection model will be used to better explain the formation of the observed cloud features on Titan. To that end, additional observations of Titan’s temperature profile and methane and ethane abundances in regions where clouds have been seen will be useful in constraining the model. Also, as described earlier, this model is well suited to understanding possible morning condensation in Titan’s stratosphere, though observations constraining the composition of the volatiles condensing in this region will be useful.

9. Summary

Steady state (i.e., clouds forming in the mean circulation) mixed clouds consisting of a methane shell surrounding an ethane core are optically thin given our current best guess for the transport rates in Titan’s lower atmosphere. Particles grow quickly to millimeter sizes and so provide a good sink for the methane vapor in the atmosphere. In steady state methane saturations rarely rise above 1.1 once cloud formation has been initiated.

Mixed clouds can form between about 10 km and the tropopause. Ethane clouds in this region immediately become nuclei for the mixed clouds, however, an ethane haze remains just above the tropopause (and the mixed clouds at the top of the troposphere are primarily composed of ethane). Additional ethane clouds are present after methane evaporates from the mixed clouds at 10 km.

The mixed clouds, which are predominantly methane except near the tropopause, can be sustained for a significant period of time without any methane resupply from the surface, indicating a surface methane source need not be constantly available. While adding nitrogen to methane lowers the vapor pressure for (liquid) cloud formation to occur, the optical thickness of such clouds is not significant compared to the supply of melting mixed cloud particles from above.
Fig. 30. Sedimentation and vapor fluxes for the base model (no source) and methane surface source models. The solid lines are the upward vapor fluxes and the symbols denote the downward particle fluxes (no source = ×, source = diamond).

Fig. 31. Comparison of growth times for methane and ethane. The plots show the time to grow cloud particles of various sizes as a function of supersaturation at an altitude of 30 km (solid lines). Lines are radii of 1 µm (triangle), 10 µm (diamond), 100 µm (square), and 1 mm (×). The initial radius (from nucleation) was assumed to be 0.1 µm. Ethane cloud particles grow at a much slower rate than methane, due to the much lower vapor pressure of ethane. Also shown (dashed lines) are the average fall times for particles of the same size (as indicated by symbol) to fall from 30 to 10 km (where the air is subsaturated with respect to methane and ethane).

Fig. 32. Cloud optical depths for several cases, base model (diamonds), surface source model (triangles), high ethane $S_{crit}$ model (squares), pure methane clouds with $S_{crit} = 1.10$ (stars), and pure methane clouds with $S_{crit} = 1.00$ (×), compared to tholin optical depth (crosses).

The fundamental balance studied here is between slow upward vapor transport by dynamics, and downward transport by sedimentation. Since the clouds contain large particles, they must be of low optical depth to achieve balance. There are several possible ways to account for optically thick clouds. Most likely, clouds simply form sporadically. Higher downward fluxes for short periods of time can also result in mass balance as discussed further in (Barth and Toon, 2004).

NASA’s Cassini mission in conjunction with ESA’s Huygens probe will soon bring us high resolution data on Titan’s atmosphere. But these will be merely snapshots. It will be the job of modeling, then, to place what we learn from the Cassini/Huygens instruments in to the general context of Titan’s daily atmospheric activity.

Acknowledgments

We thank Larry Esposito for funding through Cassini Grant JPL 961196 and the Planetary Atmospheres Program, Grant NAG5-6900, for support. We also thank Ralph Lorenz and an anonymous reviewer for their helpful suggestions.

References


