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Evidence for layered methane clouds in Titan's troposphere

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ABSTRACT

Layered methane clouds in Titan's troposphere with an upper methane ice cloud, a lower liquid methane–nitrogen cloud, and a gap in between were suggested from *in situ* measurements and ground-based observations. Here we report laboratory investigations under conditions that mimic Titan's troposphere providing a detailed picture of the cloud layers. A solid methane cloud with a nitrogen content of less than 14% and a liquid methane–nitrogen cloud with a nitrogen content of ~30% form above ~19 km and below ~16 km altitude, respectively. Contrary to previous assertions, long-lived supercooled liquid methane–nitrogen droplets can be sustained in the region in between. The results demonstrate that a cloud gap could only form in the presence of high amounts of other traces species (ethane nuclei, tholin particles, etc.).

1. Introduction

The analysis of *in situ* data from Cassini–Huygens (Niemann et al., 2005; Fulchignoni et al., 2005; Tomasko et al., 2005) suggests the presence of layered methane clouds in Titan's atmosphere between 8 and 30 km (Tokano et al., 2006; Atreya et al., 2006). This interpretation is consistent with theoretical studies (Graves et al., 2008; Barth and Toon, 2006). Similarly, ground-based observations in the infrared with the Very Large Telescope (VLT) and the W.M. Keck Observatory encompassing the Xanadu region of Titan indicate the presence of a methane ice cloud between approximately 25 and 35 km and a drizzle of liquid methane at lower elevations (Adamkovics et al., 2007). Taken together the above data suggest an upper methane ice cloud (or haze) between approximately 20 and 30 km and a lower liquid methane–nitrogen cloud between 8 and 16 km (Tokano et al., 2006; Atreya et al., 2006), perhaps with a gap in between (Tokano et al., 2006). The relative humidity of methane is approximately 95% over liquid CH_4–N_2 at 8 km (Atreya et al., 2006). It gradually approaches 100% above 8 km, with the droplets freezing at ~16 km (methane is subsaturated relative to pure methane ice in this region, with the relative humidity hovering around the 80% level). This implies a cloud or haze between 8 and 16 km that consists of liquid CH_4–N_2, with an estimated nitrogen gas content of ~20% (Tokano et al., 2006; Atreya et al., 2006). Evidence for the existence of this condensate comes from the increase in the CH_4 count rate registered by the Gas Chromatograph Mass Spectrometer (GCMS), apparently due to evaporation of liquid droplets in the heated inlet of the GCMS as the Huygens probe descended through ~16 km region (Niemann et al., 2005; Atreya et al., 2006), and by the morning drizzle inferred from the VLT and Keck Observatory data (Adamkovics et al., 2007). Evidence for the upper methane cloud above 20 km is provided by the detection of optically thin methane haze at ~21 km by the Huygens Descent Imager Spectral Radiometer (DISR) (Tomasko et al., 2005). This upper cloud is made up of almost pure solid CH_4 (Tokano et al., 2006) in accord with the phase behaviour of CH_4–N_2 mixtures (Kouvaris and Flasar, 1991). In the transition region between 16 and 20 km, it has been argued that temperatures might be too low to sustain supercooled liquid CH_4–N_2 clouds, while the methane pressure might be too low for pure CH_4 to condense. This would support the presence of a cloud gap in this transition region (Tokano et al., 2006).

We studied the condensation of methane in the laboratory in order to understand the cloud structure in Titan's atmosphere. The experiments were carried out in a low temperature aerosol cell (Firanescu et al., 2006; Signorell and Jetzki, 2007; Sigurbjörnsson and Signorell, 2008; Wang et al., 2009) under conditions that mimic the atmospheric composition, pressure, and temperature in Titan's troposphere at altitudes between 13 and 19 km. Specifically, we have attempted to address the following questions:

(i) Whether methane condensation happens at all under Titan's tropospheric conditions and, if so, what type of condensates – solid CH_4 or liquid CH_4–N_2 – can exist at different altitudes?
(ii) What is the nitrogen concentration in the aerosol particles? Can the binary mixture exist as supercooled liquid droplets above the freezing level at ~15–16 km, similar to terrestrial water clouds at temperatures below 0 °C?
(iii) What is the influence of other trace species of Titan's atmosphere on the condensation of methane?

2. Experiment

The cold methane–nitrogen atmosphere of Titan was simulated in our low temperature aerosol cell (Firanescu et al., 2006) for temperatures (78–82 K), total pressures (540–760 mbar), and methane mixing ratios (0.02–0.03 by volume) corresponding to altitudes between 19 and 13 km. The values were adjusted to match *in situ* measurements of the Huygens Atmospheric Structure Instrument (HASI) and the GCMS (Niemann et al., 2005; Fulchignoni et al., 2005; Atreya et al., 2006). To reach the low temperatures, the entire aerosol cell was immersed in liquid nitrogen. Temperatures above 78 K were realized by gently heating the cell with several heating elements (precision ±0.5 K). The cold cell was filled with nitrogen–methane gas mixtures representative of the various altitudes on Titan. Note that aerosols do not form spontaneously in such thermally equilibrated nitrogen–methane atmospheres. Instead, any condensation would happen at the cell walls since the vapour pressure over bulk phase is lower than the vapour pressure over aerosol particles due to the Kelvin effect. Aerosol formation was induced by injecting a small amount of methane gas into the centre of the cell where condensation to aerosol particles is the only possibility because the cell walls are too far away. For aerosol characterization, infrared extinction spectra were recorded *in situ* along the centre of the cold cell with a rapid-scan Fourier transform infrared spectrometer

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(time resolution 30 ms, spectral resolution 0.5 cm^{-1}), while the total pressure in the cell was monitored as a function of time. Pressure measurements provide valuable information on aerosol formation, evaporation, and on nitrogen co-condensation.

3. Results and discussion

We discuss first the results for the binary CH_4–N_2 system, which is representative of an atmosphere with no or very minor amounts of other trace species. While aerosols are formed and sustained under all conditions that mimic the region between 13 and 19 km on Titan, an abrupt change of the properties of the condensates is found for conditions representative of an altitude of ~19 km. Above this value, almost pure solid CH_4 particles are formed (Fig. 1). If pure N_2 (Fig. 1A, curve 2) is introduced into a CH_4–N_2 atmosphere (curve 1) that mimics the Titan atmosphere at about 19 km (~78 K) no aerosol formation takes place. After an initial pressure increase during injection and cooling of the additional N_2 gas (first few minutes for curve 2), the pressure in the cell simply stabilizes at a higher value due to the injected N_2 gas. The infrared spectrum in the inset confirms the absence of aerosol formation. The baseline in the inset is flat because there is no elastic scattering by particles (Bohren and Huffman, 1998). If instead of 16 mbar N_2 gas, 16 mbar CH_4 gas (Fig. 1B, curve 3) is introduced into the same CH_4–N_2 mixture (curve 1), all additional CH_4 is found to condense to particles. After an initial pressure increase during gas injection and cooling, the pressure stabilizes (curve 3) almost at the value of the original atmosphere (curve 1). The additional CH_4 gas does not increase the pressure because of the formation of CH_4 condensates. Aerosol formation is also confirmed by the slanted baseline in the infrared spectrum shown in the inset (Bohren and Huffman, 1998). In fact, the pressure decreases slightly compared with curve 1, which may imply the incorporation of a small amount of N_2 vapour into the solid particles, but this is within the range of experimental uncertainty. This subset of experiments demonstrates that almost pure solid methane aerosol particles are formed, possibly with little N_2 incorporated. From the uncertainty, we estimate an upper limit of 14% on the N_2 content.

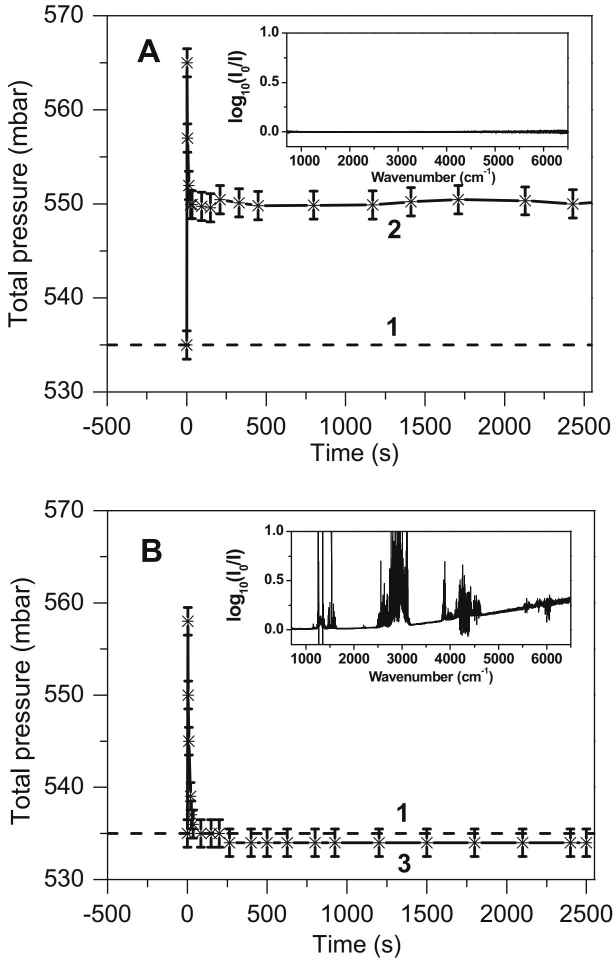

Fig. 1. Methane aerosol formation under conditions that mimic Titan's troposphere at ~19 km altitude. Shown are the total pressure as a function of time in the aerosol cell and the infrared spectra (insets). The dashed curve (1) indicates the total pressure of the CH_4–N_2 atmosphere before gas injection at 0 s. (A) Injection of pure N_2 gas does not lead to aerosol formation (curve 2). The baseline in the infrared spectrum confirms the absence of aerosols. (B) After injection of CH_4 gas, almost pure, solid CH_4 aerosols (N_2 content <14%) are formed (curve 3). Aerosol formation is also confirmed by the slanted baseline in the infrared spectrum. Note that the CH_4 infrared absorption bands of the aerosols lie underneath the saturated CH_4 gas absorptions and can thus not be exploited for analysis.

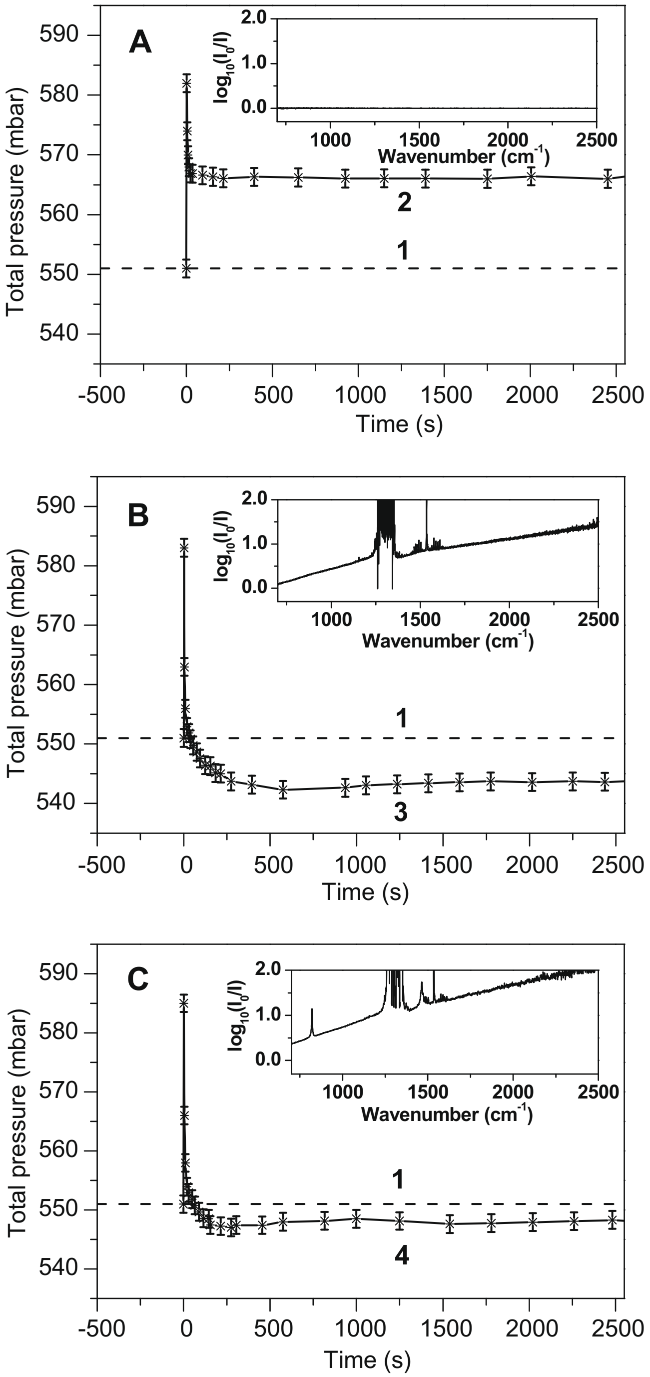

Fig. 2. Analogous to Fig. 1, but under conditions that mimic Titan's troposphere at ~17.5 km altitude. (A) No aerosol formation is observed in the control measurement where N_2 gas is injected (curve 2 and infrared spectrum). (B) Supercooled liquid CH_4–N_2 droplets with an N_2 content of 30 ± 7% are formed and sustained after injection of CH_4 gas (curve 3 and infrared spectrum). Droplets of the same composition are observed for conditions corresponding to altitudes down to ~13 km. Below ~15–16 km, the long-lived supercooled droplets turn into stable liquid droplets. (C) If small amounts of C_2H_6 nuclei are present, the supercooled phase is partially depleted (curve 4).

At conditions corresponding to altitudes below ~19 km on Titan, liquid CH_4–N_2 droplets are formed instead of pure solid CH_4 particles. Fig. 2 shows data analogous to Fig. 1, but for a Titan atmosphere at an altitude of ~17.5 km (~78.5 K). As expected, no condensation is observed for the control measurement with N_2 gas in Fig. 2A. If instead of 16 mbar N_2 gas, 16 mbar CH_4 gas is introduced into the cell, we find clear evidence for aerosol formation and incorporation of N_2 into the condensates. In this case, the total pressure (Fig. 2B, curve 3) drops well below the initial value (curve 1) after injection of CH_4. This behaviour can only be explained by inclusion of N_2 vapour into the condensates, i.e. by the formation of mixed *supercooled* CH_4–N_2 droplets. Because 78.5 K lies below the freezing level, supercooled instead of stable liquid droplets are formed under these conditions. Supercooling is confirmed by the fact that upon contact with other nuclei these droplets freeze immediately. From the known amount of CH_4 introduced and the pressure drop we calculate a nitrogen content in the CH_4–N_2 droplets of 30 ± 7%. Particle formation is again confirmed by the slanted baseline in the infrared spectrum in the inset. Scattering in the infrared spectrum of the liquid CH_4–N_2 droplets (Fig. 2B) is more pronounced than in the spectrum of the pure solid CH_4 particles (Fig. 1B). This is at least partly due to the inclusion of N_2, which leads to larger droplets and thus stronger scattering. The results in Fig. 2 demonstrate that once formed supercooled liquid CH_4–N_2 droplets could be sustained between about 19 and 15–16 km (freezing level) in Titan's atmosphere, analogous to supercooled water droplets below 0 °C in the Earth's atmosphere. Thus, contrary to previous assertions (Tokano et al., 2006), it is evidently not too cold to sustain supercooled droplets above the freezing level. We find an almost constant composition of the CH_4–N_2 droplets (nitrogen content 30 ± 7%) for all conditions down to approximately 13 km altitude in Titan, which is in agreement with the expectations from phase diagrams (Kouvaris and Flasar, 1991; Thomson et al., 1992).

The results of our laboratory simulation experiment show that in a "clean" (with little trace species) atmosphere, supercooled liquid CH_4–N_2 droplets would be long lasting since the only depletion mechanism is spontaneous freezing (Fig. 3A). However, the presence of suitable trace species such as ethane nuclei, tholin particles, or polymers of polyynes, polycyclic aromatic hydrocarbons and nitriles that could serve as heterogeneous crystallization nuclei may impact the kinetics of condensation and freezing. Such species may either inhibit the formation of long-lived supercooled droplets if they act as condensation nuclei or lead to immediate heterogeneous freezing through contact with the supercooled liquid droplets (Sigurbjörnsson and Signorell, 2008; Wang et al., 2009). The impact of other trace species depends strongly on their abundance and possibly to a lesser extent on their chemical composition (Curtis et al., 2008). High concentrations ($\gg 10^{-2}$% w/w) of impurities can rapidly and completely deplete the supercooled phase. Low concentrations ($<10^{-2}$% w/w) only lead to a partial depletion as shown in Fig. 2C (curve 4), where ethane was chosen as the only impurity with an abundance of 10^{-3} relative to CH_4, which is similar to the value in Titan's stratosphere (Vinatier et al., 2007; Flasar et al., 2005). (Ethane was chosen since it is the most abundant product of the methane photochemistry.) Compared with Fig. 2B, the pressure drops less because in the presence of ethane nuclei fewer supercooled droplets can be sustained and thus less N_2 is stored in the condensed phase under otherwise equivalent conditions. However, this conclusion is based on an ethane/methane ratio that may be too large for the troposphere.

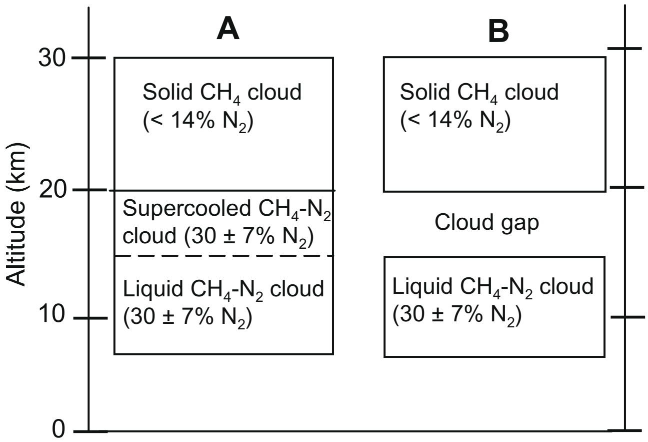

Fig. 3. Proposed structure of the methane cloud layers in Titan's troposphere. (A) In a "clean" atmosphere with low concentrations of other nuclei (ethane nuclei, tholin particles, nitriles, polymers, etc.), a single condensation region extends from 8 to 30 km. Above ~19 km, the cloud consists of almost pure solid CH_4. Supercooled liquid CH_4–N_2 droplets are sustained below this altitude down to the freezing level at ~15–16 km. Below the freezing level, liquid CH_4–N_2 droplets exist down to ~8 km. (B) Supercooled droplets can no longer be sustained in a highly "polluted" atmosphere with high concentrations of other nuclei. A cloud gap forms in between the upper solid CH_4 cloud and the lower liquid CH_4–N_2 cloud.

The C_2H_6/CH_4 ratio is roughly 10^{-3} in the stratosphere of Titan, but it has not yet been measured in the region of interest for this paper, the troposphere. However, it is possible to assess whether the stratospheric values would apply to the 10–20 km considered here. Based on the condensation curve (direct observations are not available) the condensation of ethane occurs in the lower stratosphere near Titan's tropopause. The ethane condensate would thus be expected to evaporate as it descends through the (warmer) troposphere, reducing the concentration of ethane nuclei. On the other hand, condensation of methane occurs in the middle to lower troposphere where methane concentrations are greater than in the stratosphere. As a result, the stratospheric value of C_2H_6/CH_4 used in the above experiment may be too high. In effect, the consequence of a smaller concentration of ethane nuclei and a larger concentration of methane would be a greater probability of formation of supercooled droplets, as the available ethane nuclei may be too sparse to significantly deplete the supercooled liquid CH_4–N_2 droplets in the 16–20 km altitude range (Fig. 3A). The latter was predicted and is supported by the theoretical results from Barth and Toon (2006). If the combined total of all condensed species and aerosols were large enough, it could prevent supercooling of the methane droplets or at least deplete the supercooled phase significantly, as in the above experiment with C_2H_6 alone. Such a highly "polluted" atmosphere could result in a cloud gap (Fig. 3B). On the basis of currently available data on trace species and the results from the present study, however, the latter scenario appears rather unlikely.

Although the laboratory simulations presented here pertain to the Huygens landing site for which all relevant atmospheric measurements are available, they are in general applicable to other sites and seasons on Titan with appropriate adjustments for composition and structure. However, measurements of methane abundance in the troposphere are available only in the Huygens landing site. Any variation in the atmospheric methane content and temperatures would result in changes in the altitudes of the cloud layers discussed in this paper, as was predicted previously by Lorenz and Lunine (2002) in a pre-Cassini thermodynamic model. Considering a near surface CH_4 mole fraction of 0.06 in the equatorial region and 0.02 in the polar region, with corresponding surface temperatures of 93 K and 89 K, but a latitude-independent tropopause temperature of 71 K, they found that the CH_4–N_2 freezing point was at 14 km and 19 km, respectively, in the equatorial and the polar region. Indeed, based on an analysis of radiance from the surface of Titan in the 19 μm spectral window, Cassini infrared spectrometer observations yield a zonally averaged surface temperature of 90.5 ± 0.8 K at 87°N, 3.2 K lower than in the Huygens' equatorial landing site (Jennings et al., 2009). The laboratory experiments of this paper can easily be extended once relevant data become available for other latitudes.

4. Conclusions

Our laboratory investigations provide evidence in support of layered methane clouds in the troposphere of Titan (Fig. 3), with a higher solid CH_4 cloud and a lower liquid CH_4–N_2 cloud. We find that two scenarios for the structure of these cloud layers are conceivable: a single extended condensation region (Fig. 3A) or a gap in between the solid and the liquid cloud layers (Fig. 3B). In a "clean" Titan atmosphere where supercooling is a distinct possibility in the region between ~16 and 19 km according to our results, a single extensive condensation region could extend from approximately 8 to 30 km (Fig. 3A). The phase and the chemical composition of these clouds would change rather abruptly around 19 km above which only solid particles can form. Our laboratory measurements also show that the N_2 content of the solid particles is less than 14%. Liquid CH_4–N_2 droplets with an N_2 content of 30 ± 7% can be sustained below ~19 km in a "clean" atmosphere (Fig. 3A) and below 15–16 km in a highly "polluted" atmosphere (Fig. 3B). While a highly polluted atmosphere implies the existence of a cloud gap between approximately 15–16 km and 19 km, we find that a clean atmosphere can sustain long-lived supercooled CH_4–N_2 droplets in this region analogous to supercooled water droplets in Earth's atmosphere below 0 °C.

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