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METHANE GAS STABILIZES SUPERCOOLED ETHANE DROPLETS IN TITAN'S CLOUDS

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ABSTRACT

Strong evidence for ethane clouds in various regions of Titan's atmosphere has recently been found. Ethane is usually assumed to exist as ice particles in these clouds, although the possible role of liquid and supercooled liquid ethane droplets has been recognized. Here, we report on infrared spectroscopic measurements of ethane aerosols performed in the laboratory under conditions mimicking Titan's lower atmosphere. The results clearly show that liquid ethane droplets are significantly stabilized by methane gas which is ubiquitous in Titan's nitrogen atmosphere—a phenomenon that does not have a counterpart for water droplets in Earth's atmosphere. Our data imply that supercooled ethane droplets are much more abundant in Titan's clouds than previously anticipated. Possibly, these liquid droplets are even more important for cloud processes and the formation of lakes than ethane ice particles.

Key words: planets and satellites: atmospheres

1. INTRODUCTION

Titan, Saturn's largest moon, exhibits a dense nitrogen–methane atmosphere, 1.5 times denser than that of Earth near the surface. Irradiation by sunlight and bombardment by energetic electrons in Titan's upper atmosphere lead to the formation of higher hydrocarbons, nitriles, and many other trace species (Coustenis et al. 2007). These constituents aggregate to form aerosols at various altitudes when the corresponding temperature and pressure conditions allow. Suspended in the atmosphere, they make up Titan's characteristic haze and clouds. Of special interest and importance are methane, ethane, and their mixed aerosols, as their formation mechanism, intrinsic properties, and the underlying microphysics play a crucial role in governing the cloud structure of Titan's lower atmosphere, and thus in the overall meteorological cycle on Titan (McKay et al. 1993; Atreya et al. 2006; Barth & Toon 2006; Mitri et al. 2007; Lunine & Atreya 2008; Graves et al. 2008; Tokano 2009; Cordier et al. 2009). Titan's methane–ethane clouds have been investigated by in situ measurement and ground-based observation (Tomasko et al. 2005; Porco et al. 2005; Rannou et al. 2006; Schaller et al. 2006; Griffith et al. 2006; Adamkovics et al. 2007; Brown et al. 2009; Turtle et al. 2009), as well as by theoretical modeling (Lorenz & Lunine 2002; Barth & Toon 2003, 2006; Tokano et al. 2006; Graves et al. 2008) and laboratory simulation (Signorell & Jetzki 2007; Curtis et al. 2008; Sigurbjörnsson & Signorell 2008; Wang et al. 2010; 2009).

Ethane is the third most abundant species in Titan's atmosphere after nitrogen and methane. The volume mixing ratios of nitrogen, methane, and ethane in Titan's stratosphere are 0.98, 0.014, and 1.3×10^{-5}, respectively (Coustenis et al. 2007; Niemann et al. 2005). Of these, ethane is the most likely to condense into aerosols under conditions in Titan's lower atmosphere. The properties of ethane and mixed ethane clouds have been modeled by Barth & Toon (2003, 2006) and by Graves et al. (2008). Strong evidence for ethane clouds in various regions on Titan has indeed been found, including observations from the Cassini mission (Porco et al. 2005; Rannou et al. 2006; Schaller et al. 2006; Griffith et al. 2006; Turtle et al. 2009). These studies reveal that ethane aerosols are not only a major component in Titan's clouds, but are also likely to play a significant role in the formation of tropospheric methane clouds and of lakes on Titan, such as Ontario Lacus which most likely contains ethane, in solution with methane, nitrogen, and other small hydrocarbons (Mitri et al. 2007; Stofan et al. 2007; Lunine & Atreya 2008; Brown et al. 2008; Turtle et al. 2009; Cordier et al. 2009). However, the central question of the relative importance of ice particles versus liquid and supercooled droplets in ethane clouds has not been addressed so far.

Here, we study ethane aerosols in the laboratory under conditions that mimic those in Titan's lower atmosphere in order to understand the phase behavior of ethane clouds. In particular, we address the question of how the small amount of methane gas ubiquitous in Titan's atmosphere influences the properties of ethane and mixed ethane-containing clouds. We have recently reported on properties of ethane aerosols (Sigurbjörnsson & Signorell 2008; Sigurbjörnsson et al. 2009; Wang et al. 2009). However, these investigations were performed without methane gas present in the nitrogen atmosphere. We found that under Titan's conditions pure ethane aerosols initially form supercooled droplets. In the absence of other ice nuclei (acetylene aerosols, tholin particles, etc.), i.e., if homogeneous freezing is prevalent, these droplets are rather long-lived species with a stability comparable to that of supercooled water droplets in Earth's atmosphere. In the presence of other crystallization nuclei, however, much higher freezing rates are observed. Depending on the amount of nuclei, freezing can even happen instantaneously. The present results reveal that methane gas in Titan's atmosphere indeed plays a major role in determining whether ethane clouds are liquid or solid.

2. EXPERIMENT

Ethane aerosols were generated in a low-temperature aerosol cell (Firanescu et al. 2006) that simulated the conditions in Titan's lower atmosphere (Niemann et al. 2005; Fulchignoni et al. 2005; Atreya et al. 2006). Prior to aerosol generation, the pre-cooled cell at a temperature of 78 K (corresponding to the temperature at ~20 km and ~60 km in Titan's atmosphere) was filled with methane–nitrogen gas mixtures, which reached thermal equilibrium with the cell after several minutes. The total pressure in the cell was adjusted to ~540 mbar with varying mole fractions of methane between 0 and 0.026, covering the

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typical range of mole fractions in Titan's atmosphere below about 60 km altitude. Note that under these conditions, methane cannot condense to aerosols, but remains in the gaseous state. Ethane aerosol droplets were then generated by injecting warm ethane gas into the cold cell pre-filled with the various CH_4–N_2 gas mixtures. The chosen ethane mole fractions in the range of 10^{-5} correspond to the estimated value in Titan's atmosphere (Cordier et al. 2009). The systematic variation of the methane mole fraction in the cell allowed us to demonstrate the influence of gaseous methane on the properties of ethane aerosols. To clarify the role of nitrogen gas, nitrogen was replaced by helium in a series of control experiments. Furthermore, we have repeated all experiments also in the presence of acetylene and carbon dioxide ice aerosols, respectively (number ratio C_2H_2 (or CO_2):C_2H_6 $\sim$ 1:3). These experiments simulate the presence of other trace aerosols in Titan's atmosphere that could serve as heterogeneous condensation and crystallization nuclei for ethane droplets (Barth & Toon 2003; Curtis et al. 2008; Sigurbjörnsson & Signorell 2008).

For the characterization of ethane aerosols and their temporal behavior, time-resolved (resolution 30 ms) mid-infrared extinction spectra (600–7000 cm^{-1}) were recorded in situ in the cold cell at a spectral resolution of 0.5 cm^{-1} with a Bruker IFS 66 v/S spectrometer. The CH_3 deformation mode ν_9 around 800 cm^{-1} is particularly sensitive to properties of ethane aerosols (Sigurbjörnsson & Signorell 2008; Sigurbjörnsson et al. 2009) and thus serves us in the following as the major tool for droplet/particle characterization.

3. RESULTS

First we present the results for the binary system C_2H_6–N_2 and the ternary system C_2H_6–CH_4–N_2. These mimic the behavior of ethane aerosols under "clean" conditions in Titan's atmosphere, i.e., in the absence of other trace species such as acetylene aerosols or tholin particles. Figure 1(a) shows the temporal evolution of the ν_9 mode of C_2H_6 aerosol droplets formed in a pure nitrogen atmosphere (CH_4 mole fraction is 0). We had previously reported the behavior of such binary systems (Sigurbjörnsson & Signorell 2008; Sigurbjörnsson et al. 2009). Briefly, supercooled liquid droplets are formed initially, which give rise to the structureless broad band profile in the spectra after 1 s and 217 s in panel (a). Over time, the supercooled droplets undergo phase transitions through a metastable intermediate cubic crystal phase (phase I, Sigurbjörnsson & Signorell 2008), which quickly converts into the stable monoclinic crystal structure (phase II, Sigurbjörnsson & Signorell 2008). The phase transition sets in at about 1377 s. The spectrum recorded at 1793 s shows features both from phase I and from phase II, which are converted almost completely to phase II at 2208 s.

Figures 1(b) and (c) demonstrate the influence of the presence of methane gas on the properties of ethane aerosols (ternary systems). The CH_4 mole fractions in the cell were 0.007 and $\geqslant$0.011 in panels (b) and (c), respectively (identical results were found for mole fractions of 0.011, 0.015, and 0.026). Otherwise the conditions were equivalent to panel (a). The presence of CH_4 gas in the atmosphere obviously delays the onset of crystallization of the liquid ethane droplets even for low methane content (panel (b)). By the end of the measurement at 2208 s, a significant proportion of ethane aerosol still remains in the supercooled liquid phase, exhibiting the characteristic broad infrared bands, while the onset of crystallization leads to the sharp features that superimpose the broad liquid bands. The influence of methane gas is more pronounced for higher methane mole fractions (panel (c)). In this case, the possible onset of crystallization cannot be observed on the timescale of the experiment. The band profile of ethane aerosols remains unstructured as for the supercooled liquid phase throughout the time of measurement. The results in Figure 1 clearly show that methane intervenes in the ethane crystallization processes, by stabilizing liquid ethane droplets. This can only happen as a consequence of methane inclusion into the ethane droplets during the condensation of ethane.

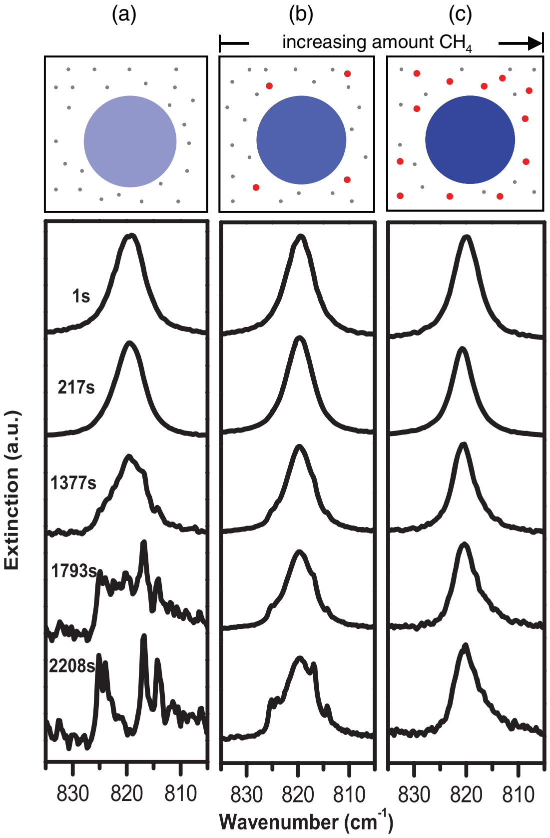

Figure 1. Homogeneous freezing of supercooled ethane clouds for cloud droplets formed in (a) a N_2 gas (gray dots) atmosphere, (b) a N_2/CH_4 gas atmosphere with a CH_4 (red dots) mole fraction of 0.007, and (c) a N_2/CH_4 gas atmosphere with a CH_4 mole fractions $\geqslant$0.011. The temporal evolution of the infrared spectra shows that the freezing rates decrease significantly in the presence of CH_4 gas. At higher CH_4 gas concentrations, more CH_4 (symbolized by darker blue shades of the droplet) is incorporated into the C_2H_6 droplets, which stabilizes the liquid droplets.

Various trace species, such as acetylene aerosols or tholin particles, are known to be present in Titan's atmosphere. Depending on their abundance these trace species might have an important influence on the crystallization dynamics of supercooled liquid ethane droplets. We found previously that the freezing rate of ethane droplets increases dramatically in the presence of appreciable amounts of other trace species (Sigurbjörnsson & Signorell 2008). This is shown here in Figure 2(a) where crystallization of supercooled ethane droplets in the presence of acetylene nuclei is monitored as a function of time. As in Figure 1(a) these experiments were performed in an otherwise pure N_2 atmosphere (no CH_4 gas). The crystallization is significantly faster in Figure 2(a) than found in Figure 1(a) due to heterogeneous freezing induced by the acetylene nuclei. In fact, freezing starts right after aerosol formation as can be seen from the spectrum measured after 1 s. The question is now whether the presence of methane gas on Titan also influences

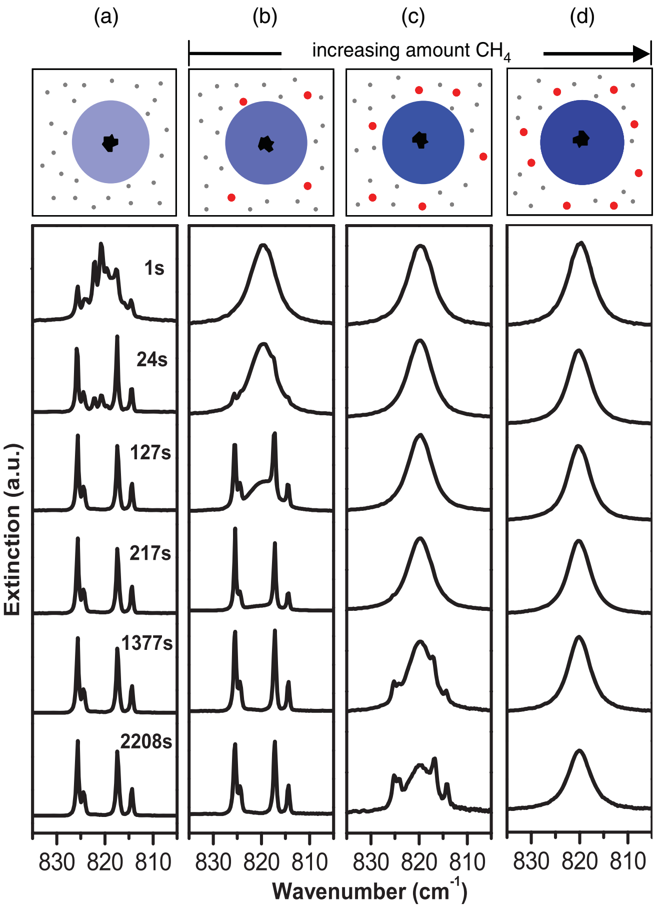

Figure 2. Analogous to Figure 1, but for heterogeneous freezing induced by the presence of acetylene aerosol particles (black nuclei in the droplets). The droplets are formed in (a) a N_2 gas (gray dots) atmosphere, (b) a N_2/CH_4 gas atmosphere with a CH_4 (red dots) mole fraction of 0.007, (c) a N_2/CH_4 gas atmosphere with a CH_4 mole fraction of 0.011, and (d) a N_2/CH_4 gas atmosphere with a CH_4 mole fractions $\geqslant$0.015. The temporal evolution of the infrared spectra shows that liquid C_2H_6 droplets are stabilized by CH_4 gas even in the presence of other aerosol particles. More CH_4 (darker blue shades) in the C_2H_6 droplets leads to slower freezing. Identical results are found if acetylene particles are replaced by carbon dioxide particles.

the heterogeneous freezing kinetics of ethane droplets similar to the observations for homogeneous freezing described above. Figures 2(b)–(d) show the corresponding results for methane mole fractions of 0.007, 0.011, and $\geqslant$0.015, respectively, when acetylene aerosols act as heterogeneous crystallization nuclei (mole fractions of 0.015 and 0.026 show identical results). The impact of methane on the freezing kinetics of ethane droplets is evident. Increasing amounts of methane gas (panels (b)–(d)) slow down the heterogeneous crystallization of the droplets significantly. The trend is the same as observed for homogeneous freezing in Figure 1.

While acetylene is one of the most abundant trace species in Titan's atmosphere, we have also performed the heterogeneous freezing experiments using carbon dioxide aerosol instead of acetylene. The major motivation was to ascertain that the effects observed for acetylene are generic and not particular to this single substance. We found the same effects for both types of crystallization nuclei. Moreover, the CO_2 infrared bands allow us to gather information about what happens to the crystallization nuclei during the freezing process. As a result of strong vibrational exciton coupling, the appearance of CO_2 infrared bands is exceptionally sensitive to phase changes and to mixing with other substances (ethane) (Firanescu et al. 2006; Sigurbjörnsson et al. 2009). Figure 3 shows that the CO_2 nuclei are not affected by the phase transition and do not mix with ethane either. The latter aspect is particularly noteworthy since mixing with ethane would radically change the role of the crystallization nuclei.

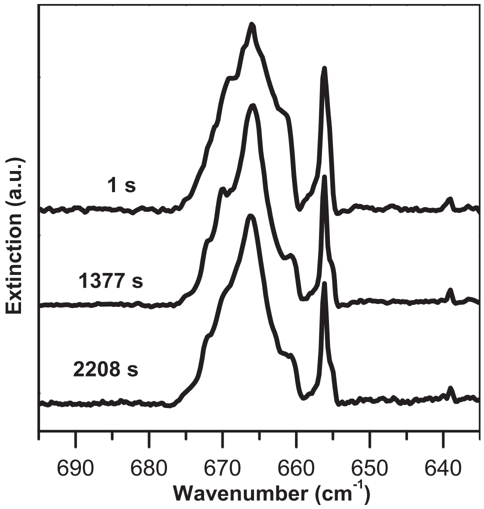

Figure 3. Infrared spectra in the region of the bending mode of the CO_2 ice nuclei during the crystallization of ethane (Figure 2). The spectra are stable over time demonstrating that CO_2 ice particles indeed act as crystallization nuclei, i.e., do not mix with ethane (Sigurbjörnsson et al. 2009). The same band shapes were observed for all different methane mole fractions in Figure 2.

Lastly, we have repeated all experiments for the above-described binary, ternary, and quaternary systems replacing N_2 with He to clarify the possible influence of N_2. We found that crystallization is slightly faster in He compared with N_2. However, compared to the influence of CH_4 gas (mole fractions <0.026), the influence of N_2 gas (mole fractions >0.974) is much less important. N_2 gas clearly does not play the major role in the stabilization of ethane droplets in contrast to CH_4 gas. There are several possible explanations why crystallization is slightly faster in He. It could be that a small amount of nitrogen is incorporated into the ethane droplets. From additional experiments (Wang et al. 2010), we estimate an upper limit of 7% on the N_2 content (experimental uncertainty) in a pure N_2 atmosphere. Alternative explanations would be the different particle formation conditions caused by different diffusion behavior, cooling efficiency, etc. in the two different gases.

4. DISCUSSION

The laboratory simulations presented here demonstrate that the stability of supercooled ethane droplets in an N_2/CH_4 atmosphere like Titan's is predominantly governed by the presence of methane gas. Inclusion of methane gas (probably with some N_2) into ethane droplets upon droplet formation depresses the freezing point of the droplets, lowers the vapor pressure, and dramatically decreases the freezing rates of supercooled droplets. Both, freezing point depression and freezing rates, depend on the amount of methane in the droplets. From preliminary experiments analogous to those described in Wang et al. (2010), we estimate the maximum CH_4 content in the droplets to be less than 20%. Assuming ideal behavior, this would correspond to a maximum freezing point depression of ~5 K (freezing point of pure C_2H_6 is 90 K).

In the absence of methane gas (Figure 1(a)), we determine homogeneous volume freezing rate constants for supercooled ethane droplets of $\sim 10^8$ cm^{-3} s^{-1} (Sigurbjörnsson & Signorell 2008). Homogeneous rates are only relevant in a "clean" atmosphere. In the presence of other trace aerosols (a "polluted" atmosphere), heterogeneous freezing is the main mechanism. Heterogeneous freezing rate constants can be orders of magnitude higher depending on the amount of heterogeneous crystallization nuclei, which at high concentrations can even lead to instantaneous freezing as in Figure 2(a). The presence of CH_4 gas completely changes this behavior. Homogeneous as well as heterogeneous freezing rates (Figures 1(b–c) and 2(b–d)) decrease by orders of magnitude so that supercooled liquid ethane droplets become very long-lived species. Without CH_4 gas, 90% of 1 μm ethane droplets would be frozen within about an hour in a "clean" atmosphere and immediately in a "polluted" atmosphere. Under the influence of CH_4 gas, droplets of the same size remain liquid for many hours or even days, depending on the methane abundance and the presence of "pollutants."

Methane gas makes freezing of ethane droplets more difficult and thus much less likely to occur on Titan than previously assumed. A comparison with the temperature profile and the composition of Titan's atmosphere shows that the present results are relevant to all regions of Titan's lower atmosphere, indicating the importance of liquid ethane droplets. The pronounced effects we observed further imply that in many regions of Titan's lower atmosphere supercooled droplets might be more important than ethane ice particles for various cloud processes, including the formation of tropospheric methane clouds, and possibly even for the formation of Titan's lakes. In light of our results, cloud models need to be revised to account for supercooled liquid ethane droplets, which might substantially change our understanding of Titan's cloud structure. Considering the much cited analogies between Titan's and Earth's atmosphere, it is worth noting that the stabilization of ethane droplets by the presence of methane gas has no equivalent for water droplets in Earth's atmosphere. There is no ubiquitous gaseous component in sufficient abundance that could co-condense with water. In a more general sense, those differences to Earth derive from the absence of a strongly hydrogen-bonding cloud constituent in Titan's atmosphere.

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