Microphysical Properties of Hydrocarbon Aerosols Relevant to Titan’s Clouds

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Image credit: NASA/JPL/ Space Science Institute
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Hydrocarbon Aerosols in Titan’s Lower Atmosphere

Titan’s Atmosphere

0 km – 60 km
1466 mbar – 42 mbar
94 K – 71 K

Image credit: NASA/JPL/ Space Science Institute
CH₄  • Composition of the condensates (CH₄ or CH₄/N₂)?
    • Phase of the condensates
      (solid, liquid, supercooled: freezing kinetics)?

C₂H₆  • Solid, liquid, supercooled: freezing kinetics?
    • Influence of CH₄ gas on the freezing kinetics?

C₂H₂, CO₂  • Role as crystallization nuclei?

C₃H₈, C₂H₄, ...  • Role as antifreeze?
Experiment

infrared spectroscopy combined with low temperature aerosol cell
Bath Gas Cooling

Generation of Volatile Aerosols

PARAMETER:
- Sample Concentration
- Bath Gas Pressure
- Bath Gas Temperature

JPC A, 2890, 110, 2006
Twin Chamber Cell

- Twin chamber to study reactions, phase transitions
- Chemically resistant interior
- Temperature homogeneity ~1K (T < 298K)
- Optics with improved transmission
- High-vacuum tight
RESS (Rapid Expansion of Supercritical Solutions)

Generation of Non-Volatile Aerosols

Solvent: Supercritical CO$_2$
- $T < 500$ K
- $p < 40$ MPa

Solute

Mach Disk

Infrared

Rev. Sci. Instr, 2005
Aerosol Irradiation Chamber
Photochemical Aerosol Formation

Teflon Bag
UV Light
Infrared
Infrared Spectroscopy of Aerosols

a) SIZE AND SURFACE EFFECTS

b) SHAPE

c) INTERNAL STRUCTURE
Composition/Phase/Architecture

d) DYNAMIC PROCESSES
Reactions, Phase Transitions, Mixing
Molecular Model
goes beyond standard approaches such as Mie theory or DDA
Vibrational Exciton Approach

\[ \hat{H} = \hat{H}_0 + \sum_{i,j} \mu_i^+ A_{ij} \mu_j \]

with \( A_{ij} = -\frac{1}{2} \left( \lambda_{ij} + \sum_k \lambda_k \alpha_k \lambda_{jk} \right) \)

and \( \lambda_{ij} = \frac{(1 - \delta_{ij})}{4\pi\epsilon_0 R_{ij}^3} (3e_{ij} e_i^+ - 1) \)

\[ C(t) = g(t) \sum_{k,m,l,n} \langle k_m | \mu_{km} e^{-i\hat{H}t/\hbar} \mu_{ln} | l_n \rangle \]

Annu. Rev. Phys. Chem, 60, 2009
CPL, 260, 371, 2003
JCP, 2707, 118, 2003
Degeneracy Lifted, Delocalization of Eigenfunctions

infrared band

no coupling
coupling

E

E=0

ν / cm\(^{-1}\)
**Shape Effects: CO₂ Aerosols**

**CO₂ Clouds on Mars**

Mars Express

- Particle Size: 10 - 100 nm
- Number of Molecules per Particle: $10^5 - 10^8$

Van der Waals forces

Credit: NASA
Particle Shape

Low bath gas pressure

High bath gas pressure

No Shape Effects in Infrared Spectra of Homogeneously Mixed Particles!

\[ \tilde{\nu} / \text{cm}^{-1} \]

Annu. Rev. Phys. Chem, 60, 2009
Architecture: Core-Shell Particles

PCCP, 4149, 8, 2006 // JCP, 184301, 128, 2008
Cubic shell $\rightarrow$ doublet structure

Cube
Particle Phase: Acetylene Aerosols

Orthorhombic crystal structure
→ Three peaks

Polycrystalline structure
→ Broad peak

PCCP, 7924, 12, 2010
Nucleation
freezing of supercooled droplets
Freezing Kinetics of Droplets

Volume vs. Surface Crystallization?

Size-Dependent Crystallization Dynamics

PCCP, 187, 11, 2009
Results for Titan Aerosols
**Methane Aerosols**

Titan \quad Earth

- total pressure \sim total pressure
- $N_2$ major component \sim $N_2$ major component
- $\text{CH}_4$ \sim $\text{H}_2\text{O}$
- temperature \ll temperature
Cassini-Huygens Mission
Tokano et al., Nature, 442, 2006

Ground-based Observations
Adamkovics et al. Science, 318, 2007

Modeling
Barth & Toon, Icarus, 182, 2006

LETTERS

Methane drizzle on Titan
Tetsuya Tokano¹, Christopher P. McKay², Fritz M. Neubauer¹, Sushil K. Atreya³, Francesca Ferri⁴, Marcello Fulchignoni⁵,⁶ & Hasso B. Niemann⁷

Saturn’s moon Titan shows landscapes with fluvial features¹ suggestive of hydrology based on liquid methane. Recent efforts in understanding Titan’s methane hydrological cycle have focused on the existence of liquid hydrocarbons in the atmosphere, which could be crucial for the formation of bodies such as lakes or seas on Titan. The study suggests that the methane drizzle is a significant process in the cycle, contributing to the redistribution of methane and its role in the formation of liquid bodies. The behavior of methane in the atmosphere is complex due to the presence of other gases, such as nitrogen, which can affect the stability of methane and its phase transitions.
Methane Cloud Structure

**Suggestion:**
In situ observations by Huygens, Earth-based observations, and cloud modeling

**Our Laboratory Studies:**
Icarus, 779, 212, 2011
Icarus, 787, 206, 2010
JPC A, 11129, 113, 2009

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Altitude (km)

- **Solid CH₄ cloud, N₂ < 14%**
- **Cloud gap**
- **Liquid CH₄-N₂ cloud**
- **Supercooled Liquid CH₄-N₂ cloud, N₂ ~ 30%**
  - Possibly depleted
- **Liquid CH₄-N₂ cloud, N₂ ~ 30%**
Degree of Saturation for CH$_4$/N$_2$ Condensation from Monte Carlo Calculations

**Experimental Huygens Data:**
Niemann et al., Nature, 779, 438, 2005

saturation: $85 \pm 6\%$

Icarus, 779, 212, 2011

Experimental Huygens Data:

saturation: $100 \pm 6\%$
Evidence for a Polar Ethane Cloud on TITAN

solid particles
liquid / supercooled droplets
Freezing of Supercooled C$_2$H$_6$ Droplets

- **Supercooled liquid droplets**
- **Crystalline particles**

**Homogeneous Freezing**
1 µm droplet freezes in 1 hour

**Heterogeneous Freezing**
1 µm droplet freezes immediately

**Analysis of freezing kinetics**

PCCP, 6211, 10, 2008
Influence of CH$_4$ Gas on Freezing Kinetics of C$_2$H$_6$ droplets

CH$_4$: Antifreeze

1µm droplet freezes within days:
Supercooled C$_2$H$_6$ droplets are “long-lived” species

Lowers the freezing point:
extends the liquid region

Planetary and Space Science, in press, 2011
Nitrogen versus Helium Atmosphere

Atmosphere:
He gas + CH$_4$ gas

Atmosphere:
N$_2$ gas + CH$_4$ gas

Planetary and Space Science, in press, 2011
Trace species $\text{C}_3\text{H}_8$, $\text{C}_2\text{H}_4$: Antifreeze

Co-condensation of propane and ethylene stabilizes the ethane droplets against freezing

$\text{C}_3\text{H}_8 + \text{C}_2\text{H}_6$

$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$

JPC A, 1129, 113, 2009
Trace aerosols $\text{C}_2\text{H}_2$, $\text{CO}_2$: Heterogeneous Crystallization
Trace species $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_6$, $\text{CO}_2$: Heterogeneous Crystallization

Pure $\text{C}_2\text{H}_2$ aerosols:

$\text{C}_2\text{H}_2$ polycrystalline

$\text{C}_2\text{H}_2$ aerosols as condensation nuclei:

$\text{C}_2\text{H}_2$ crystalline

Planetary and Space Science, in press, 2011
PCCP, 7924, 12, 2010
Freezing Mechanisms

Immersion freezing

Contact freezing

Planetary and Space Science, in press, 2011
Hydrocarbon Aerosols in Titan’s Troposphere

CH$_4$ Aerosols

- Solid CH$_4$ cloud
- Supercooled CH$_4$-N$_2$ cloud
- Liquid CH$_4$-N$_2$ cloud

C$_2$H$_6$ Aerosols

- Supercooled droplets
- Solid particles

“long-lived” species because of CH$_4$ gas

“long-lived” species because of N$_2$ gas