Infrared Spectroscopy of Hydrocarbon Aerosols at Cryogenic Temperatures with Application to Titan

by

Eva Kathrin Lang

Diplom, University of Potsdam, Germany, 2008

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

in

THE FACULTY OF GRADUATE STUDIES
(Chemistry)

The University of British Columbia
(Vancouver)

July 2013

© Eva Kathrin Lang, 2013
Abstract

The atmosphere of Saturn’s moon Titan features hydrocarbon clouds, for example those composed of methane and ethane, the properties of which are not completely understood. To improve the understanding of Titan’s clouds, studies of the phase behavior of pure and mixed hydrocarbon aerosols were carried out.

The aerosol particles were generated in a bath gas cooling cell under conditions representative of Titan’s lower atmosphere (78 K, 500-1000 mbar). The freezing and crystallization behavior of the aerosol particles were studied using rapid-scan infrared spectroscopy and the observed phases identified by comparison with thin film measurements.

Under the studied conditions ethane forms long-lived supercooled liquid droplets that are stabilized against freezing by the incorporation of methane and nitrogen gas, which are ubiquitous in Titan’s atmosphere. The extent of the stabilization increases with increasing methane partial pressure. The studies demonstrate that supercooled ethane droplets could have an appreciable lifetime and might play an important role in the condensation of methane in Titan’s atmosphere.

The influence of the presence of aerosols of other atmospheric components (acetylene, carbon dioxide, and water) on the freezing of supercooled hydrocarbon droplets was studied in heterogeneous nucleation experiments. The aerosols were found to accelerate the crystallization of hydrocarbon aerosols to differing degrees depending on their composition.

Numerous hydrocarbons exist as minor atmospheric components and might be of importance for Titan’s clouds and lakes. Propane was found to form long-lived supercooled droplets at 78 K, which did not crystallize even in the presence of heterogeneous nuclei. \( n \)-Butane and \( n \)-pentane initially form amorphous-annealed particles. \( n \)-Butane particles were observed to
undergo two phase transitions and \( n \)-pentane particles one. The surface and volume nucleation rate constants, \( J_V \) and \( J_S \), were determined for all three of these transitions and are likely to be important for models of Titan's clouds.

Taken together, these studies provide a detailed picture of the phase behavior of hydrocarbon aerosols under conditions relevant to Titan. This is important for understanding cloud formation and the radiation budget on Titan. Furthermore, the recorded spectroscopic signatures provide a reference for astrophysical studies concerned with the detection and characterization of aerosols in Titan’s atmosphere.
Preface

Chapter 3 was published as:

- C. C. Wang, E. K. Lang, and R. Signorell, *Astrophys. J. Lett.* (2010), 712, L40-L43. Methane gas stabilizes supercooled ethane droplets in Titan’s clouds. The experiments were performed by C. C. Wang and E. K. Lang. The research project was designed by R. Signorell. The manuscript was prepared by C. C. Wang and R. Signorell.

- E. K. Lang, K. J. Knox, C. C. Wang, and R. Signorell, *Planet. Space Sci.* (2011), 59, 722-732. The influence of methane, acetylene and carbon dioxide on the crystallization of supercooled ethane droplets in Titan’s clouds. The experiments were performed by E. K. Lang and K. J. Knox. The research project was designed by R. Signorell. The manuscript was prepared by E. K. Lang, K. J. Knox, and R. Signorell.

- D. Luckhaus, G. Firanescu, E. K. Lang, G. N. Patey, and R. Signorell, accepted for publication in *Mol. Phys.* (2013). The composition of ternary C$_2$H$_6$/CH$_4$/N$_2$ cloud droplets under Titan conditions: Monte Carlo simulations and experiment. The programs were written by G. Firanescu and D. Luckhaus. The calculations were performed by D. Luckhaus, G. Firanescu, and E. K. Lang. G. N. Patey provided theoretical support. R. Signorell designed the research project and wrote the manuscript.

Chapter 4 was published as:

- E. K. Lang, K. J. Knox, and R. Signorell, *Planet. Space Sci.* (2012), 75, 56–68. Phase behavior of propane and n-pentane aerosol particles under conditions relevant to Titan. The experiments and data analysis were performed by E. K. Lang and K. J. Knox. The
research project was designed by R. Signorell. The manuscript was prepared by E. K. Lang, K. J. Knox, and R. Signorell.

Chapter 5 has been accepted for publication in *J. Phys. Chem. A*:

- E. K. Lang, K. J. Knox, T. Momose, and R. Signorell, (2013). Infrared spectroscopy and phase behavior of *n*-butane aerosols and thin films at cryogenic temperatures. The experiments and data analysis were performed by E. K. Lang with support from K. J. Knox. The research project was designed by R. Signorell. T. Momose provided access to his thin film set-up. The manuscript was prepared by E. K. Lang, K. J. Knox, and R. Signorell.

Chapter 6 was published as:

# Table of Contents

Abstract ................................................................. ii

Preface ................................................................. iv

Table of Contents ...................................................... vi

List of Tables .......................................................... xii

List of Figures .......................................................... xiv

List of Abbreviations .................................................. xxiv

List of Symbols ........................................................ xxvi

Acknowledgments ....................................................... xxvii

1 Introduction ........................................................... 1

1.1 Aerosols .............................................................. 1

1.2 Titan vs. Earth: An Overview ................................... 3

1.3 A Short Summary of Titan Research Activities ............... 6

1.3.1 Observations ...................................................... 6

1.3.1.1 From the Discovery until the First Space Mission .... 6

1.3.1.2 Voyager I and II .............................................. 6

1.3.1.3 Space and Ground-based Observations ................ 7

1.3.1.4 Cassini-Huygens ............................................ 8

1.3.2 Atmospheric Models ............................................ 9
1.3.3 Laboratory Measurements ........................................ 10
1.4 Condensable Hydrocarbons in Titan’s Atmosphere .............. 11
1.4.1 Atmospheric Abundances of Hydrocarbons .................. 11
1.4.2 Titan’s Methane and Ethane Clouds .......................... 12
   1.4.2.1 Potential Importance of Supercooled Liquid Particles ... 12
   1.4.2.2 Potential Importance of Heterogeneous Freezing ......... 14
1.4.3 The Role of Other Potential Condensates ..................... 18
   1.4.3.1 Coating of Tholins .................................. 18
1.4.4 The Potential Role of Lakes .................................. 19
1.5 Thesis Outlook ..................................................... 20

2 Experimental ......................................................... 22
2.1 Infrared Measurements of Hydrocarbon Aerosols ............... 22
   2.1.1 Cooling Cell .............................................. 22
   2.1.2 Sample Preparation ....................................... 23
   2.1.3 Injection Methods ......................................... 24
   2.1.4 Acquisition of Spectra .................................... 25
   2.1.5 Experimental Conditions and Execution .................... 26
2.2 Infrared Measurements of Hydrocarbon Thin Films ............. 27
   2.2.1 Instrumental Set-up ....................................... 27
   2.2.2 Sample Preparation ....................................... 28
      2.2.2.1 Vapor Deposition .................................... 28
      2.2.2.2 Optical Cell Condensation ........................... 29
   2.2.3 Acquisition of Spectra .................................... 29

3 The Influence of Methane, Acetylene and Carbon Dioxide on the Crystal-
   lization of Supercooled Ethane Droplets in Titan’s Clouds ...... 30
3.1 Introduction ...................................................... 30
3.2 Experimental ..................................................... 32
3.3 Results and Discussion .......................................... 33
3.3.1 Overview of Spectroscopic Signatures of Pure and Mixed Aerosols  
3.3.2 Spectroscopic Studies of the Homogeneous Crystallization of Ethane and the Influence of Methane Gas  
3.3.3 Influence of Aerosols of Trace Species on \( \text{C}_2\text{H}_6 \) Crystallization  
3.3.4 Influence of Freezing Mechanism on \( \text{C}_2\text{H}_6 \) Crystallization  
3.3.5 Role of \( \text{N}_2 \) in the Freezing Dynamics of \( \text{C}_2\text{H}_6 \) Droplets  
3.4 Conclusions  

4 Phase Behavior of Propane and \( \text{n-Pentane} \) Aerosol Particles Under Conditions Relevant to Titan  
4.1 Introduction  
4.2 Experimental  
4.3 Results and Discussion  
4.3.1 Propane Aerosols  
4.3.1.1 Propane Aerosols in \( \text{He} \) and \( \text{N}_2 \) Bath Gas  
4.3.1.2 Propane Aerosols in the Presence of \( \text{C}_2\text{H}_2, \text{CO}_2, \) and \( \text{H}_2\text{O} \)  
4.3.2 \( \text{n-Pentane} \) Aerosols  
4.3.2.1 \( \text{n-Pentane} \) Aerosols in \( \text{He} \) and \( \text{N}_2 \) Bath Gas  
4.3.2.2 Crystallization Kinetics in \( \text{N}_2 \) Bath Gas  
4.3.2.3 Crystallization in the Presence of \( \text{C}_2\text{H}_2, \text{CO}_2, \) and \( \text{H}_2\text{O} \)  
4.4 Conclusions  

5 Infrared Spectroscopy and Phase Behavior of \( \text{n-Butane} \) Aerosols and Thin Films at Cryogenic Temperatures\(^*\)  
5.1 Introduction  
5.2 Experimental Methods and Analysis of Phase-Transition Kinetics  
5.2.1 Aerosol Measurements  
5.2.2 Thin Film Measurements  
5.2.3 Kinetic Analysis of Aerosol Phase Transitions  
5.3 Results and Discussion
5.3.1 IR Spectra of Thin Films of \( n \)-Butane

5.3.1.1 Amorphous \( n \)-Butane

5.3.1.2 Crystalline \( n \)-Butane

5.3.1.3 Liquid \( n \)-Butane

5.3.2 Identification of the Phases of the Aerosol Particles

5.3.2.1 Phase of \( n \)-Butane Aerosols Immediately after Formation

5.3.2.2 Phase of \( n \)-Butane Aerosols after the First Transition

5.3.2.3 Phase of \( n \)-Butane Aerosols after the Second Transition

5.3.3 Phase Transitions of Pure \( n \)-Butane Aerosols

5.3.3.1 Phase Transition from Amorphous-Annealed to Phase II

5.3.3.2 Phase Transition from Phase II to Phase III

5.3.4 Phase Transitions of Mixed Aerosol Systems: \( n \)-Butane Mixed with \( C_2H_2, CO_2 \), or \( H_2O \)

5.3.4.1 First Phase Transition

5.3.4.2 Second Phase Transition

5.4 Summary

6 Infrared Extinction Spectra of Aerosols with Relevance to Planetary and Lunar Atmospheres

6.1 Introduction

6.2 Experimental

6.3 Spectra of Pure Aerosols

6.3.1 Methane

6.3.2 Ethane

6.3.3 Propane

6.3.4 \( n \)-Butane

6.3.5 \( n \)-Pentane

6.3.6 Ethylene / Ethene

6.3.7 Acetylene / Ethyne

6.3.8 Carbon Dioxide
B.3 Non-linear Fit to Determine $J_V$ and $J_S$ ........................................ 178

C Sensitivity Analysis for the Determination of the Rate Constant $J$ .... 179
   C.1 Particle Size Distribution ...................................................... 180
      C.1.1 Complex Refractive Index Data ..................................... 180
      C.1.2 Integration Band for Scaling ......................................... 180
      C.1.3 Geometric Standard Deviation $\sigma$ ................................. 181
   C.2 $\bar{P}_{\text{exp}}(t)$ ............................................................. 182
List of Tables

Table 2.1 Overview of hydrocarbons of interest ........................................... 24
Table 3.1 The freezing points of pure C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} mixtures ..................... 41
Table 4.1 Vibrational band positions for C\textsubscript{3}H\textsubscript{8} films and aerosol in cm\textsuperscript{-1} .................. 63
Table 4.2 Vibrational band positions for liquid and solid \(n\)-C\textsubscript{5}H\textsubscript{12} films and aerosols in cm\textsuperscript{-1} at various temperatures ................................. 73
Table 5.1 Observed vibrational band positions in cm\textsuperscript{-1} for thin films of \(n\)-C\textsubscript{4}H\textsubscript{10} in various phases between 20 and 137 K ......................... 110
Table 6.1 Substances for which aerosol spectra are presented, with normal melting points of bulk substances and examples of atmospheres in which the aerosols are thought or have been confirmed to be present .................. 113
Table 6.2 Summary of spectral data presented: ASCII filename, substance and relevant publication(s), dominant particle phase, time relative to injection (s), bath gas pressure (mbar), temperature at which recorded (K), spectral range (cm\textsuperscript{-1}) ................................................................. 125
Table 7.1 Overview of solid \(n\)-alkanes from C\textsubscript{1}-C\textsubscript{5} at pressures \(\leq 1\) bar ................................. 127
Table 7.2 Observed vibrational frequencies of the phases of a thin film of C\textsubscript{2}H\textsubscript{6} between 20-95 K ................................................................. 133
Table 7.3 Observed vibrational frequencies of the phases of a thin film of C\textsubscript{3}H\textsubscript{8} between 20-100 K and viscous liquid aerosol particles at 78 K ....................... 137
List of Figures

Figure 1.1  Left: Atmospheric temperature profile of Titan as measured by the Huygens Atmospheric Structure Instrument (HASI). The horizontal lines mark the mesopause (152 K at 490 km), the stratopause (186 K at 250 km) and the tropopause (70.43 K at 44 km). Furthermore the altitude of the main haze layer (∼ 250 km) and the main cloud layers (∼ 8-30 km and ∼ 60 km) are indicated. Right: U.S. Standard Atmosphere of Earth as of 1975. The horizontal lines mark the mesopause (187.9 K at 86 km), the stratopause (270.7 K at 47 km) and the tropopause (217.7 K at 11 km).

Figure 1.2  The energy of embryo formation ΔG as a function of embryo radius r. For r > r_{crit} spontaneous growth of the embryo occurs.

Figure 2.1  Sketch of the experimental set-up to study aerosol ensembles, consisting of a FTIR spectrometer and a custom made cooling cell.

Figure 2.2  Injection schemes for gas samples: (i) one-component and premixed injection, (ii) sequential injection with a time delay Δt between the two pulses.

Figure 2.3  Experimental set-up for thin film measurements at cryogenic temperatures.

Figure 3.1  IR spectra of (A) supercooled C_2H_6 aerosol droplets in N_2 gas, (B) supercooled C_2H_6 aerosol droplets in a N_2/CH_4 gas mixture with y_{CH_4} = 0.007, (C) mixed C_2H_6/C_2H_2 aerosols in N_2 gas, and (D) mixed C_2H_6/CO_2 aerosols in N_2 gas. The spectra were recorded ∼ 1 s after injection of the sample gases into the cooling cell.
Figure 3.2 The temporal evolution (top to bottom) of the $\nu_9$ fundamental during homogeneous freezing of supercooled C$_2$H$_6$ droplets formed in (A) pure N$_2$ gas, (B) a CH$_4$/N$_2$ atmosphere with $y_{CH_4} = 0.007$, and (C) a CH$_4$/N$_2$ atmosphere with $y_{CH_4} = 0.015$. The presence of CH$_4$ gas decreases the freezing rates. ................................................................. 37

Figure 3.3 Analogous to Fig. 3.2 but for the $\nu_6$ fundamental. The sharp peaks below 1370 cm$^{-1}$ in parts B and C arise from rovibrational transition of cold CH$_4$ gas (see also Fig. 3.1B). Note that the C$_2$H$_6$ bands reduce in signal over time because of diffusion of the particles out of the IR beam. ................. 38

Figure 3.4 Analogous to Fig. 3.2, but for the $\nu_8$ fundamental. The additional sharp peaks in parts B and C (not present in part A) arise from rovibrational transitions of cold CH$_4$ gas. ................................................................. 38

Figure 3.5 IR spectra of crystalline C$_2$H$_6$ aerosol particles: (A) monoclinic phase II, (B) cubic phase I. The slanted baseline of the $\nu_8$ band in part B is due to elastic light scattering by the particles. ................................................................. 39

Figure 3.6 The temporal evolution (top to bottom) of the $\nu_9$ fundamental during heterogeneous freezing of supercooled C$_2$H$_6$ droplets induced by C$_2$H$_2$ aerosols. The droplets were formed in (A) pure N$_2$ gas, (B) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.007$, (C) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.011$, and (D) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.025$. The presence of CH$_4$ gas decreases the freezing rates. ................................................................. 42

Figure 3.7 Analogous to Fig. 3.6, but for the $\nu_6$ band. Only part A shows features of C$_2$H$_6$ phase I at 1365 cm$^{-1}$. The sharp peaks below 1370 cm$^{-1}$ in B-D arise from rovibrational transition of cold CH$_4$ gas (see also Fig. 3.1B). ................. 43

Figure 3.8 Analogous to Fig. 3.6, but for the $\nu_8$ band at 1465 cm$^{-1}$. The additional sharp peaks in B-D (not present in A) arise from rovibrational transitions of cold CH$_4$ gas. ................................................................. 43
Figure 3.9  The temporal evolution (top to bottom) of the $\nu_9$ fundamental during heterogeneous freezing of supercooled C$_2$H$_6$ droplets induced by CO$_2$ aerosols. The droplets were formed in (A) pure N$_2$ gas, (B) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.007$, (C) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.011$, and (D) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.025$. The presence of CH$_4$ gas decreases the freezing rates. .................................................................

Figure 3.10 Analogous to Fig. 3.9, but for the $\nu_8$ band. The additional sharp peaks in B-D (not present in A) arise from rovibrational transitions of cold CH$_4$ gas. .................................

Figure 3.11 Time evolution (top to bottom) of (A) the $\nu_5$-C$_2$H$_2$ band and (B) the $\nu_2$-CO$_2$ band during the crystallization of C$_2$H$_6$ in mixed C$_2$H$_6$/C$_2$H$_2$ and C$_2$H$_6$/CO$_2$ aerosols, respectively. The C$_2$H$_2$ cores have a crystalline orthorhombic structure at $t = 1$ s. Over time, they convert into a polycrystalline form. The CO$_2$ cores have a cubic crystalline structure which does not change over time. ....................................................... .................................

Figure 3.12 Illustration of crystallization of supercooled C$_2$H$_6$ droplets (open circles) in the presence of C$_2$H$_2$ aerosols (filled black circles) via (A) immersion and (B) contact freezing of supercooled C$_2$H$_6$ in the presence of C$_2$H$_2$ nuclei (black circles). The particle clouds spread down the cell over time. .................. .................................

Figure 3.13 Temporal evolution the $\nu_9$ band of C$_2$H$_6$ in a N$_2$/CH$_4$ gas atmosphere with $y_{CH_4} = 0.011$ for (A) premixed injection of C$_2$H$_2$/C$_2$H$_6$, (B) separate but simultaneous injection of C$_2$H$_2$ and C$_2$H$_6$ ($\Delta t = 0$ ms), and (C) sequential injection of C$_2$H$_2$ followed by C$_2$H$_6$ ($\Delta t = 5920$ ms). Different freezing rates indicate a different nucleation mechanism. ................................. .................................
Figure 3.14 The $\nu_5$-bending mode of C$_2$H$_2$ recorded immediately after C$_2$H$_6$ injection for (A) premixed injection of C$_2$H$_2$/C$_2$H$_6$, (B) separate but simultaneous injection of C$_2$H$_2$ and C$_2$H$_6$, and (C) sequential injection of C$_2$H$_2$ followed by C$_2$H$_6$ ($\Delta t = 5920$ ms). The spectra in parts A and B exhibit features of orthorhombic C$_2$H$_2$, which is caused by annealing due to condensation of C$_2$H$_6$ onto the C$_2$H$_2$ nuclei. The spectrum in part (C) shows the broad features of polycrystalline C$_2$H$_2$. Annealing is not possible in this case because C$_2$H$_2$ and C$_2$H$_6$ do not form core-shell structures.

Figure 3.15 Temporal evolution the $\nu_9$ band of C$_2$H$_6$ for pure supercooled C$_2$H$_6$ droplets in (A) He and (B) N$_2$. Crystallization is slightly faster in He than in N$_2$.

Figure 4.1 Infrared spectra of (A) C$_3$H$_8$ aerosols in N$_2$ (800 mbar) at 78 K and (B) mixed C$_3$H$_8$/C$_2$H$_2$ aerosols (C$_3$H$_8$:C$_2$H$_2 = 4:1$) in N$_2$ (800 mbar) at 78 K.

Figure 4.2 Time evolution of the IR spectra of C$_3$H$_8$ aerosols in (A) He (800 mbar) and (B) N$_2$ (800 mbar) (C$_3$H$_8$:bath gas = $\sim 10^{-5}$:1) at 78 K in the region of the $\nu_5$ and $\nu_4$ bands. The time after droplet/particle formation is indicated for each spectrum in part A and is the same for the adjacent spectrum in part B.

Figure 4.3 Time evolution of the IR spectra of mixed C$_3$H$_8$/C$_2$H$_2$ aerosols (C$_3$H$_8$:C$_2$H$_2 = 2:1$) in N$_2$ (800 mbar) at 78 K. A: Region of the $\nu_5$ and $\nu_4$ bands of C$_3$H$_8$. B: Region of the $\nu_5$ bands of C$_2$H$_2$ with the $\nu_{26}$ band of C$_3$H$_8$ at 747 cm$^{-1}$. The time after droplet/particle formation is indicated for each spectrum in part A and is the same for the adjacent spectrum in part B.

Figure 4.4 IR spectra of (A) n-C$_5$H$_{12}$ aerosols in N$_2$ and (B) crystalline n-C$_5$H$_{12}$ aerosols in He (n-C$_5$H$_{12}$:bath gas = $\sim 10^{-5}$:1) recorded immediately ($t = 1$ s) after injection of n-C$_5$H$_{12}$ gas into the cold bath gas. The cell temperature was 78 K in both cases.
Figure 4.5  Comparison of the temporal evolution of IR spectra of \( n\text{-C}_5\text{H}_{12} \) aerosol condensates in He (A.1 and B.1) and \( \text{N}_2 \) (A.2 and B.2) (\( n\text{-C}_5\text{H}_{12} \):bath gas = \( \sim 10^{-5}:1 \)) at a temperature of 78 K and 800 mbar cell pressure. The two frequency ranges that are the most characteristic for the phase transition are shown. The time after the formation of the aerosol condensates is indicated for each spectrum in A.1 and A.2; in B.1 (B.2) times for the individual spectra are as for those in A.1 (A.2). The dashed lines at \( t = 49 \) s in A.2 and B.2 are reconstructed spectra (see Section 4.3.2.2).

Figure 4.6  IR spectra of (A) liquid bulk \( n\text{-C}_5\text{H}_{12} \) at room temperature, (B) liquid \( n\text{-C}_5\text{H}_{12} \) aerosol droplets formed just above 143 K, (C) \( n\text{-C}_5\text{H}_{12} \) aerosol condensates formed immediately (\( t = 1 \) s) after injection of warm \( n\text{-C}_5\text{H}_{12} \) gas into the cold cell at 78 K, and (D) crystalline \( n\text{-C}_5\text{H}_{12} \) particles at 78 K after crystallization is completed. \( \text{N}_2 \) was used as the bath gas for all aerosols.

Figure 4.7  A: Logarithm of the fraction of uncrystallized particles as a function of time \( \bar{P}_{\text{exp}}(t) \). Dots with error bars: Experimental data, solid line: Fit for pure volume nucleation (\( J_S(T) = 0 \)), dashed line: Fit for pure surface nucleation (\( J_V(T) = 0 \)). The two fits are for \( \sigma = 1.6 \). B: Typical time evolution of the mean particle radius \( r \) for \( \sigma = 1.6 \). Dots: Experimental data, line: Polynomial fit to experimental data.

Figure 4.8  Time-dependent IR spectra in the region between 1440 and 1480 cm\(^{-1}\) recorded during the heterogeneous crystallization of \( n\text{-C}_5\text{H}_{12} \) aerosols in the presence of (A) \( \text{C}_2\text{H}_2 \) (\( \text{C}_5\text{H}_{12}:\text{C}_2\text{H}_2 = 2:1 \)), (B) \( \text{CO}_2 \) (\( \text{C}_5\text{H}_{12}:\text{CO}_2 = 2:1 \)), and (C) \( \text{H}_2\text{O} \) (\( \text{C}_5\text{H}_{12}:\text{H}_2\text{O} = 1.4:1 \)). The experiments were performed in \( \text{N}_2 \) bath gas at a pressure of 800 mbar. The time after particle formation is indicated in panel B for each spectrum and increases from top to bottom.
Figure 4.9  Comparison between premixed (A.1 and B.1) and sequential injection (A.2 and B.2) for heterogeneous crystallization of $n$-C$_5$H$_{12}$ aerosols in the presence of C$_2$H$_2$. The time-delay for the sequential injection was $\Delta t = 1$ s, with valve opening times of 0.5 s. Panels A.1 and A.2 show $n$-C$_5$H$_{12}$ bands in the region between 1440 and 1480 cm$^{-1}$. Panels B.1 and B.2 depict the region of the bending vibration of C$_2$H$_2$. The experiments were performed in N$_2$ bath gas at a pressure of 800 mbar. The time after particle formation is indicated in panel A.1 and B.1 for each spectrum; in A.2 (B.2) the times for the individual spectra are as for those for panel A.1 (B.1).

Figure 5.1  IR transmission spectra collected from a thin film of $n$-C$_4$H$_{10}$ between 20 and 137 K. Spectra A to D were obtained from a vapor-deposited sample on a ZnSe substrate. Spectra E to G were obtained from a sample of $n$-C$_4$H$_{10}$ contained within a closed cell. The spectra in the rightmost three panels have been scaled as indicated for clarity. All spectra are baseline corrected.

Figure 5.2  A comparison of the spectrum of (A) $n$-C$_4$H$_{10}$ aerosol particles collected immediately after particle formation at 78 K with the spectra of a thin film of (B) amorphous-annealed $n$-C$_4$H$_{10}$ at 45 K, (C) amorphous $n$-C$_4$H$_{10}$ at 20 K, and (D) liquid $n$-C$_4$H$_{10}$ at 137 K.

Figure 5.3  A comparison of the spectrum of liquid $n$-C$_4$H$_{10}$ aerosol particles at $T > 135$ K (A) with the spectrum of a thin film of liquid $n$-C$_4$H$_{10}$ at $T = 137$ K (B).

Figure 5.4  A comparison of the spectrum of $n$-C$_4$H$_{10}$ aerosol particles after completion of the first observed phase transition at $T = 78$ K (A) with the spectrum of a thin film of $n$-C$_4$H$_{10}$ in phase II at $T = 83$ K (B).

Figure 5.5  A comparison of the spectrum of $n$-C$_4$H$_{10}$ aerosol particles after completion of the second observed phase transition at $T = 78$ K (A) with the spectrum of a thin film of $n$-C$_4$H$_{10}$ in phase III at $T = 85$ K (B).
Figure 5.6  Time evolution of the IR spectrum of $n$-$C_4H_{10}$ aerosol particles during the first observed phase transition at $T = 78$ K in $N_2$ (A) and He (B). The bands shown are those that are the most sensitive to the phase of the particles. The time after particle formation is indicated for each spectrum in the leftmost frame and is the same for the adjacent frames. ........................................ 98

Figure 5.7  Typical time evolution of the mean particle radius $r(t)$ in He (open circles) and $N_2$ (closed circles). .......................................................... 100

Figure 5.8  Logarithm of the fraction of particles that remain in the initial phase as a function of time $ln(\bar{P}_{exp}(t))$ for the first (A) and second (B) observed phase transitions. Closed circles with error bars: Experimental data, solid line: Fit for pure volume nucleation $(J_S(T) = 0)$, dashed line: Fit for pure surface nucleation $(J_V(T) = 0)$. The two fits were calculated using $\sigma = 1.6$. In part B $t = 0$ s is equivalent to a time of 120 s after particle formation. Please note that the magnitude of the negative error bar shown has been reduced by using symmetric error bars for a total of three data points ($t = \sim 95$ s in A and $t = \sim 3600$ s and $\sim 5000$ s in B) for clarity. .......................... 100

Figure 5.9  Time evolution of the IR spectrum of $n$-$C_4H_{10}$ aerosol particles during the second observed phase transition at $T = 78$ K in $N_2$ (A) and He (B). The bands shown are those that are the most sensitive to the phase of the particles. The time after the start of the phase transition is indicated for each spectrum in the leftmost frame and is the same for the adjacent frames. The time after particle formation is shown in parenthesis for the first spectrum in each part. .......................................................... 102
Figure 5.10  Time evolution of the IR spectrum of $n$-C$_4$H$_{10}$ aerosol particles during the first (A.1 and A.2) and second (B.1 and B.2) observed phase transition at $T = 78$ K in N$_2$, for pure $n$-C$_4$H$_{10}$ particles (A.1 and B.1) and mixed $n$-C$_4$H$_{10}$/CO$_2$ particles prepared using pre-mixed injection (A.2 and B.2). The time after the start of the phase transition is indicated for each spectrum and the time after particle formation is shown in parenthesis for the first spectrum in B.1 and B.2.  

Figure 5.11  Typical time evolution of the mean particle radius $r(t)$ in N$_2$ (closed circles) and He (open circles) for mixed $n$-C$_4$H$_{10}$/CO$_2$ aerosol particles ($n$-C$_4$H$_{10}$:CO$_2$ = 4:1).  

Figure 6.1  IR extinction spectra of solid CH$_4$ aerosols for particles consisting of (A) amorphous CH$_4$, $T < 91$ K, (B) phase I CH$_4$, 20.4 K < $T < 91$ K, and (C) a core of phase II CH$_4$ with phase I CH$_4$ present at the surface, $T = 8$ K. The slanted baseline in this spectrum arises from light scattering by large particles.  

Figure 6.2  IR extinction bands ($\nu_3$ at $\sim 3010$ cm$^{-1}$ and $\nu_4$ at $\sim 1300$ cm$^{-1}$) of solid CH$_4$ aerosols for particles consisting of (A) amorphous CH$_4$, $T < 91$ K, (B) phase I CH$_4$, 20.4 K < $T < 91$ K, and (C) a core of phase II CH$_4$ with phase I CH$_4$ present at the surface, $T = 8$ K.  

Figure 7.1  IR spectra collected from a thin film of C$_2$H$_6$ between 20 and 92 K. Spectra A to C were obtained by vapor deposition of C$_2$H$_6$ gas on a ZnSe substrate at 20 K followed by temperature increase. Spectra D and E were obtained by injection of C$_2$H$_6$ gas into an enclosed optical cell at 140 K and subsequent cooling. All spectra are baseline corrected.  

Figure 7.2  IR spectrum of (A) C$_2$H$_6$ aerosol particles crystallized in phase II and (B) of supercooled liquid C$_2$H$_6$ after particle formation. Both spectra were obtained at 78 K. The CH-stretching region from 3050-2800 cm$^{-1}$ was obtained at a lower concentration than the fingerprint region between 1550-800 cm$^{-1}$.  

xxi
Figure 7.3  IR spectra collected from a thin film of C\textsubscript{3}H\textsubscript{8} between 20 and 100 K (A to E) and of supercooled viscous liquid C\textsubscript{3}H\textsubscript{8} aerosol particles formed at 78 K (F). Spectra A to C were obtained by vapor deposition of C\textsubscript{3}H\textsubscript{8} on a ZnSe substrate at 20 K followed by temperature increase. Spectra D and E were obtained by injecting C\textsubscript{3}H\textsubscript{8} gas into an enclosed optical cell at 100 K and subsequent cooling. All spectra are baseline corrected except for the aerosol spectrum.

Figure 7.4  IR spectra collected from a thin film of n-C\textsubscript{5}H\textsubscript{12} between 20 and 115 K. Spectra A to C were obtained by vapor deposition of n-C\textsubscript{5}H\textsubscript{12} gas on a ZnSe substrate at 20 K followed by temperature increase. Spectra D and E were obtained by injecting n-C\textsubscript{5}H\textsubscript{12} gas into an enclosed optical cell at \(\sim\) 200 K and subsequent cooling. Spectrum F is the bulk liquid measured at room temperature with an ATR FTIR. Spectra A to E are baseline corrected.

Figure 7.5  Observed phases of n-C\textsubscript{5}H\textsubscript{12} aerosol particles at 78 K in N\textsubscript{2} as bath gas. A: Crystal phase in all-\textit{trans} configuration. The crystal phase of the aerosols fits the crystal phase of the thin film obtained from the amorphous structure (Fig. 7.4C) best. B: Disordered phase that forms immediately after particle formation. The disordered aerosol phase fits the amorphous-annealed phase at 45 K of the thin film (Fig. 7.4B) best.

Figure 8.1  Vertical profile of the liquid droplet composition in Titan’s lower atmosphere as simulated with the PPR78 EOS model. \(x\) are the condensed phase mole fractions of the respective substance (N\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}) multiplied by 100. 5

Figure A.1  Optical path length of the cooling cell depending on the number of passes.

Figure B.1  The solid curve is the experimental spectrum, the dashed curve is the spectrum obtained from linear decomposition.
Figure B.2 Calculated (blue) and experimental (red) spectra of \( n-C_5H_{12} \) at 78 K at \( \sim 100 \) s after sample injection and particle formation and the time-dependent mean particle size \( r(t) \) (insert). The calculated spectra represent the lower and upper limit for the mean particle radius, 0.046 and 0.052 nm, respectively. The intensity of the slanted baseline depends on the particle size and the particle number concentration.
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACP</td>
<td>Aerosol Collector Pyrolyser</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud Condensation Nucleus/Nuclei</td>
</tr>
<tr>
<td>CIRS</td>
<td>Composite Infrared Spectrometer</td>
</tr>
<tr>
<td>DISR</td>
<td>Descent Imager/Spectral Radiometer</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>DWE</td>
<td>Doppler Wind Experiment</td>
</tr>
<tr>
<td>EOS</td>
<td>Equation Of State</td>
</tr>
<tr>
<td>GCMS</td>
<td>Gas Chromatograph and Mass Spectrometer</td>
</tr>
<tr>
<td>HASI</td>
<td>Huygens Atmospheric Structure Instrument</td>
</tr>
<tr>
<td>HST</td>
<td>Hubble Space Telescope</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GG</td>
<td>Gauche-Gauche rotamer of n-pentane</td>
</tr>
<tr>
<td>IN</td>
<td>Ice Nucleus/Nuclei</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IRIS</td>
<td>Infrared Interferometer Spectrometer</td>
</tr>
<tr>
<td>ISO</td>
<td>Infrared Space Observatory</td>
</tr>
<tr>
<td>ISS</td>
<td>Imaging Science Subsystem</td>
</tr>
<tr>
<td>LN2</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>MC</td>
<td>Monte-Carlo</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>MCT</td>
<td>Mercury-Cadmium-Telluride</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular-Dynamics</td>
</tr>
<tr>
<td>mid-IR</td>
<td>Mid-Infrared</td>
</tr>
<tr>
<td>RSS</td>
<td>Radio Science System</td>
</tr>
<tr>
<td>SSP</td>
<td>Surface Science Package</td>
</tr>
<tr>
<td>SWS</td>
<td>Short Wave Spectrometer</td>
</tr>
<tr>
<td>TG</td>
<td>Trans-Gauche rotamer of (n)-pentane</td>
</tr>
<tr>
<td>TT</td>
<td>Trans-Trans rotamer of (n)-pentane</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UVS</td>
<td>Ultraviolet Spectrometer</td>
</tr>
<tr>
<td>VIMS</td>
<td>Visual and Infrared Mapping Spectrometer</td>
</tr>
<tr>
<td>VLE</td>
<td>Vapor Liquid Equilibrium</td>
</tr>
<tr>
<td>VLT</td>
<td>Very Large Telescope</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>Methane</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>Acetylene</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>Ethane</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>Propane</td>
</tr>
<tr>
<td>(n)-C(_4)H(_10)</td>
<td><em>normal</em>-Butane</td>
</tr>
<tr>
<td>C(_4)H(_10)</td>
<td>Butane and its isomers</td>
</tr>
<tr>
<td>(n)-C(_5)H(_12)</td>
<td><em>normal</em>-Pentane</td>
</tr>
<tr>
<td>C(_5)H(_12)</td>
<td>Pentane and its isomers</td>
</tr>
</tbody>
</table>
# List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_V )</td>
<td>Volume nucleation rate constant (cm(^{-3}) s(^{-1}))</td>
</tr>
<tr>
<td>( J_S )</td>
<td>Surface nucleation rate constant (cm(^{-2}) s(^{-1}))</td>
</tr>
<tr>
<td>( P_{exp}(t) )</td>
<td>Fraction of uncrystallized particles as a function of time</td>
</tr>
<tr>
<td>( r(t) )</td>
<td>Time dependent mean radius (nm)</td>
</tr>
<tr>
<td>( S )</td>
<td>Supersaturation ratio</td>
</tr>
<tr>
<td>( T_{boil} )</td>
<td>Boiling point temperature (K)</td>
</tr>
<tr>
<td>( T_{cryst} )</td>
<td>Crystallization temperature (K)</td>
</tr>
<tr>
<td>( T_{fus} )</td>
<td>Melting point temperature (K)</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Glass transition temperature (K)</td>
</tr>
<tr>
<td>( T_{trans} )</td>
<td>Transition temperature (K)</td>
</tr>
<tr>
<td>( T_{triple} )</td>
<td>Triple point temperature (K)</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>Degree of supercooling (K)</td>
</tr>
<tr>
<td>( x )</td>
<td>Mole fraction in the condensed phase</td>
</tr>
<tr>
<td>( y )</td>
<td>Mole fraction in the gas phase</td>
</tr>
<tr>
<td>( \Delta G )</td>
<td>Free energy of formation (kJ)</td>
</tr>
<tr>
<td>( \Delta H_{pure} )</td>
<td>Heat of fusion of a pure substance (kJ mol(^{-1}))</td>
</tr>
<tr>
<td>( \Delta H_{fus} )</td>
<td>Heat of fusion (kJ mol(^{-1}))</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Geometric standard deviation</td>
</tr>
<tr>
<td>( \sigma_{l,s} )</td>
<td>Surface tension at the liquid-solid interface (N m(^{-1}))</td>
</tr>
</tbody>
</table>
Acknowledgments

First and foremost I would like to thank Prof. Ruth Signorell for her support and the opportunity to conduct my Ph.D. in her research group.
I am deeply grateful to Dr. Kerry J. Knox for her support, her encouragement, and all the lively discussions we had throughout my Ph.D. I would especially like to thank Kerry for her time, patience, suggestions, support and encouragement during the final months of writing this thesis.
I would like to thank Dr. George Firanescu, Dr. Chia. C. Wang, and Dr. David Luckhaus for their collaboration.
Many thanks go to Prof. Takamasa Momose for the opportunity to perform thin film measurements in his lab, and to Cindy Toh, Jun Miyazaki, and Pavle Djurucanin for their assistance.
Finally, I would like to thank my parents, Julius and Ulrike; my friends here in Vancouver, especially Katja, Jess, and Anna-Lena; and the Signorell group, for their support and friendship.
Chapter 1

Introduction

This thesis describes studies of the phase behavior of hydrocarbon aerosols at cryogenic temperatures, in particular the freezing of supercooled aerosol droplets, under conditions relevant to the atmosphere of Saturn’s moon Titan. Fourier transform infrared spectroscopy can be used for the study of intrinsic particle properties, such as phase, size, and architecture, and their changes over time. Here the focus is on the phase. In this chapter a brief introduction on aerosols is given, followed by a comparison of the atmospheres of Earth and Titan. A short overview of space missions, laboratory research, and modeling presents past and ongoing Titan research activities. Finally the aims of this research, specifically in the light of Titan’s clouds, are presented, and a summary of the studies in this thesis is provided. In this thesis aerosols are defined as any liquid or solid particles suspended in a gas; the term “aerosols” is used to refer to cloud condensates in Titan’s atmosphere, and is not restricted to the aerosols making up Titan’s haze layers, which are commonly referred to as Titan aerosols.

1.1 Aerosols

Aerosols are colloidal systems. They are composed of either liquid or solid particles dispersed in a gas, usually air. Aerosols are ubiquitous in the Earth’s atmosphere and have natural and anthropogenic sources such as salt aerosols from sea spray or soot particles from fossil fuel burning, respectively. Aerosols influence the Earth’s radiation balance by effects that are differentiated into direct, indirect, and semi-direct effects. Aerosols directly modify the radiation balance by absorption and scattering of solar radiation, and indirectly by altering
cloud albedo and cloud cover, for example by acting as cloud condensation nuclei (CCN).\textsuperscript{9,10} The semi-direct effect is described as the decrease in low-level cloud cover due to an increase in atmospheric temperatures and a decrease in the relative humidity caused by the absorption of radiation by tropospheric aerosols.\textsuperscript{11} These effects influence the Earth’s radiation budget and climate and possibly affect atmospheric circulation and precipitation patterns.\textsuperscript{12} However, the magnitude of these effects is difficult to quantify and highly uncertain due to the variability of aerosols in size and composition as well their atmospheric loading which is spatially and temporally fluctuating.\textsuperscript{10,13}

Scattering and absorption of radiation by aerosol particles depends on particle intrinsic properties such as size, composition, shape, and structure. The elastic scattering of light by particles much smaller than the light’s wavelength (particle diameter $d_p <<$ wavelength $\lambda$) is called Rayleigh scattering with backward and forward scattering being equal in intensity.\textsuperscript{14} On the other hand, Mie scattering describes the scattering behavior of spherical particles that have approximately the same size as $\lambda$ ($d_p \approx \lambda$), which results in strong forward scattering. Mie theory describes the interaction of an electromagnetic wave with a sphere and includes absorption and scattering.\textsuperscript{4} Absorption and scattering behavior are strongly dependent on the particle size and the complex refractive index ($m = n + ik$), in which the real part ($n$) primarily relates to scattering and the imaginary part ($k$) primarily relates to absorption. With knowledge of the complex refractive index, Mie theory can be used to predict extinction spectra of spherical aerosols, which are the result of absorption and scattering.\textsuperscript{4}

Aerosol particles can range in size from nanometers to several hundred micrometers. Aerosol particle sizes are classified into three major modes: (i) Aitken or nucleation mode ($d_p < 0.1 \mu m$), (ii) accumulation mode (0.1 $\mu m < d_p < 2.5 \mu m$), and (iii) coarse mode ($d_p > 2.5 \mu m$).\textsuperscript{14} Scattering of incoming solar radiation is found to be dominated by the accumulation mode, whereas the contribution of the coarse mode is smaller and that of the Aitken mode is negligible.\textsuperscript{14}

Absorption and scattering by aerosol particles depend on the complex refractive index which in turn depends on particle composition and structure. The composition of aerosol particles can be complex. They can be composed of pure absorbing or non-absorbing materials
or a mixture of both. Non-absorbing materials scatter incoming solar radiation back into space, leading to negative radiative forcing (i.e. surface cooling), whereas absorbing materials can lead to positive radiative forcing (i.e. warming), partly offsetting aerosol scattering.11

Aerosols and cloud condensates are not only ubiquitous in the Earth’s atmosphere but also in the atmospheres of other planetary or lunar bodies where they can have similar effects. Methane (CH$_4$), ethane (C$_2$H$_6$) and acetylene (C$_2$H$_2$) together with higher hydrocarbons, nitriles, non-volatile organic aerosols, and many other trace species, are frequently found in our solar system, such as on Neptune, Jupiter, Uranus, Venus, and Titan.15–19 On Jupiter, for example, the existence of ammonia (NH$_3$) and water (H$_2$O) clouds has been confirmed whereas on Venus sulfuric acid (H$_2$SO$_4$) aerosols have been found.16,20 Like on Earth, aerosols on these planets and moons influence atmospheric processes and properties. The focus of the present thesis is the hydrocarbon aerosols that can potentially form on Titan, the largest moon of Saturn. Of particular interest is the phase behavior of these aerosol particles.

1.2 Titan vs. Earth: An Overview

Titan’s atmosphere consists of ~98% nitrogen and ~1.4% methane in the stratosphere, and ~95% nitrogen and ~5% methane at the surface.2 The surface pressure is ~1467 mbar and is closer to the Earth’s atmospheric pressure than that of any other celestial body.1 At Titan’s equator the surface temperature is ~93.65 K. This is close to the triple point of methane ($T_{trip} = 90.69$ K),21 and thus methane can exist in the gaseous, liquid, and solid form in Titan’s atmosphere, as can water on Earth. This results in a methane cycle similar to the hydrological cycle on Earth.22,23 Methane creates a dynamic tropospheric meteorology on Titan that is comparable to the water-based meteorology of Earth including evaporation, cloud formation, precipitation, and seasonal changes.23,24 On Titan’s surface hydrocarbon lakes are present in the polar regions and fluvial features such as stream networks and shorelines indicate the existence of flowing liquids.25

Titan is enshrouded in a thick organic haze layer which is the result of Titan’s rich methane and nitrogen photochemistry that leads to the formation of saturated and unsaturated hydrocarbons and nitriles that condense, agglomerate, and form haze particles which subsequently
Figure 1.1: Left: Atmospheric temperature profile of Titan as measured by the Huygens Atmospheric Structure Instrument (HASI).\textsuperscript{1,2} The horizontal lines mark the mesopause (152 K at 490 km), the stratopause (186 K at 250 km) and the tropopause (70.43 K at 44 km). Furthermore the altitude of the main haze layer (∼ 250 km) and the main cloud layers (∼ 8–30 km and ∼ 60 km) are indicated. Right: U.S. Standard Atmosphere of Earth as of 1975.\textsuperscript{3} The horizontal lines mark the mesopause (187.9 K at 86 km), the stratopause (270.7 K at 47 km) and the tropopause (217.7 K at 11 km).

Titan’s troposphere experiences a methane driven greenhouse warming of ∼ 22 K that is offset by ∼ 10 K due to aerosol cooling caused by Titan’s haze.\textsuperscript{26,27} Titan’s haze and methane abundance determine Titan’s vertical temperature structure that, although much colder, mirrors that of Earth and is shown in Fig\textsuperscript{1,1,13} Titan’s thermosphere extends between ∼ 1020-500 km altitude. The mesopause is found around 490 km with an atmospheric temperature and pressure of 152 K and $2 \times 10^{-3}$ mbar. The temperature increases down to the stratopause, found around 250 km (∼ 186 K, 0.3 mbar). The temperature decreases towards lower altitudes and reaches its minimum of 70.4 K with an atmospheric pressure of 115 mbar at the tropopause at 44 km.\textsuperscript{1,30}

Compared to Earth, Titan’s atmosphere extends to much higher altitudes.\textsuperscript{27} In the equatorial region the Earth’s tropopause, for example, is found at ∼ 17 km and Titan’s at ∼ 44 km.\textsuperscript{1,31}
much smaller than the approximately 70 K temperature difference on Earth. On Earth and on Titan the tropopause functions as a cold trap that limits the transport of water and methane, respectively, into the stratosphere.\textsuperscript{32} In the case of Titan the cold trap can lead to the condensation of photochemical products such as gaseous ethane and propane that are transported downwards from the upper atmosphere.\textsuperscript{33}

The photochemical destruction of methane is irreversible due to hydrogen loss into space and hydrogenation of unsaturated compounds.\textsuperscript{34,35} The origin of methane in Titan’s atmosphere is not entirely clear.\textsuperscript{36} It is suggested that either a special phase in Titan’s history is currently underway or that methane is replenished.\textsuperscript{37} If methane is not replenished then it would be depleted in about $10^7$ years and Titan’s atmosphere would eventually collapse due to decreasing atmospheric temperatures and the condensation of nitrogen.\textsuperscript{38} If methane is replenished it is probably from Titan’s surface or interior. One explanation is that methane is stored as clathrate (methane trapped within the crystal structure of water ice) in Titan’s interior and is released by outgassing and through cryovolcanism, which transports material from the moon’s interior to its surface.\textsuperscript{38}

Though no liquid and only very little gaseous water is present in Titan’s atmosphere, the rocks found on Titan’s surface are presumably water ice.\textsuperscript{39} Furthermore, a liquid water ocean with a few percent of ammonia might exist under Titan’s crust.\textsuperscript{32,40} The possible existence of liquid water, despite below the surface, and Titan’s rich methane-nitrogen photochemistry that forms prebiotic molecules,\textsuperscript{4} such as hydrogen cyanide (HCN), makes Titan interesting to astrobiologists and useful in the study of the origin of life on Earth.\textsuperscript{41}

With an active meteorological system and a methane “hydrological” cycle, and a similar atmospheric surface pressure, temperature profile, and atmospheric composition (major component N$_2$), Titan is more similar to Earth than any other planet or moon in our solar system. With an atmosphere similar to that of the primitive Earth, Titan offers the opportunity to study an atmosphere that might resemble the Earth’s atmosphere before life emerged, including chemical and physical processes.\textsuperscript{32,42,43}

\textsuperscript{4}Prebiotic molecules are considered to be the precursors of life on Earth.
1.3 A Short Summary of Titan Research Activities

1.3.1 Observations

1.3.1.1 From the Discovery until the First Space Mission

Titan was first discovered in 1655 by the Dutch astronomer Christian Huygens. In 1903, José Comas y Solá was the first to suspect that Titan has an atmosphere; this was confirmed by Gerard Kuiper in 1944. Kuiper used ground-based spectroscopic methods and found evidence for the existence of methane on Titan.

It was not until the early 1970s that Titan drew fresh interest due to a series of new discoveries from infrared observations and brightness temperature determinations. Molecular hydrogen and gaseous $C_2H_6$, $C_2H_2$, and ethylene ($C_2H_4$) were detected. Following polarization observations of Titan, the existence of an opaque cloud layer and an optically thick absorbing aerosol or photochemical haze was suggested. Khare and Sagan suggested that these particles were similar to the reddish-brown material they obtained from irradiation of cosmically-relevant gases and that these particles were responsible for Titan’s orange colour.

1.3.1.2 Voyager I and II

Voyager 1 and 2 were two identical spacecrafts both launched in 1977 to study the outer planets of the solar system. The spacecrafts carried a series of instruments including narrow-angle and wide-angle cameras (Imaging Science System, ISS), a radio science system (RSS), an infrared interferometer spectrometer (IRIS, 2.5-50 $\mu m$), and an ultraviolet spectrometer (UVS).

With the Voyager 1 and 2 flybys in 1980 and 1981, respectively, the existence of gaseous $C_2H_6$, $C_2H_2$, and $C_2H_4$ was confirmed, and other gas-phase atmospheric constituents identified, such as HCN. The abundances of many atmospheric gas species including methane and ethane were determined from infrared spectra. Results from the ultraviolet spectrometer, radio occultation, and the infrared spectrometer showed that Titan’s atmosphere was predominantly made of nitrogen (82-94%), with methane as a minor constituent (6% varying with altitude).
The Voyager flybys gathered data that enabled the determination of Titan’s physical properties, such as surface pressure and temperature.\textsuperscript{58} While the existence of clouds and aerosols was expected prior to the flybys,\textsuperscript{47,51,52} it was found that a deep haze layer enshrouded the entire moon at an altitude of around 250 km with a second haze layer approximately 100 km above the first one.\textsuperscript{59,60} The Voyagers could not probe to the surface since the haze was absorbing in the UV.\textsuperscript{28,29} Titan’s methane “windows” are in the near-infrared, for example at 1.08, 1.28, and 2.0 \(\mu\text{m}\), and the Voyagers did not carry any near-infrared instruments.\textsuperscript{61,62} Therefore, the surface properties and the structure of the troposphere remained unknown.\textsuperscript{28} It was suspected that the haze layer most likely consisted of particles formed from organic molecules that were produced photochemically in the upper atmosphere, as previously suggested by Khare and Sagan.\textsuperscript{53} These organic molecules would then condense, coagulate and aggregate into aerosol particles at lower altitudes and form Titan’s haze.

1.3.1.3 Space and Ground-based Observations

In the 25 years between the Voyager flybys in 1980 and 1981 and the arrival of the Cassini-Huygens spacecraft in the Saturnian system in 2004, research on Titan was growing. Combining the obtained Voyager data with thermodynamic and atmospheric models,\textsuperscript{62–64} and based on the abundance of methane and ethane in the atmosphere and on their stability, the existence of methane clouds and rain,\textsuperscript{65–67} as well as a global ethane ocean were proposed.\textsuperscript{68–70} The number of space and ground-based observations had also significantly increased due to technological progress. The first images of Titan showing surface features were taken by the Hubble Space Telescope in 1994 and 1995.\textsuperscript{71} Water vapor in Titan’s atmosphere was discovered in 1997 with the short wave spectrometer (SWS) of the Infrared Space Observatory (ISO).\textsuperscript{72} Ground-based observations were primarily performed in the near infrared region with telescopes using adaptive optics such as the Keck II telescope (Keck Observatory, Mauna Kea, Hawaii) or the Very Large Telescope (VLT) (European Space Observatory, La Silla, Chile).\textsuperscript{73,75} These ground-based observations led to the first detections of methane clouds on Titan.\textsuperscript{67,76–78}

\footnote{A methane window is defined as a wavelength range in the spectrum of methane where it is weakly absorbing.}
1.3.1.4 Cassini-Huygens

More than 20 years after the Voyager flybys, the Cassini-Huygens spacecraft entered the Saturnian system in July 2004. On January 14, 2005 the Huygens probe landed on Titan, finally providing long-awaited in situ data on Titan’s atmosphere and surface. Since then, the Cassini orbiter has been orbiting around Saturn and continues to provide valuable data on Saturn and its moons. Since its arrival in 2004 more than 90 flybys of Titan by Cassini have occurred.

The Cassini orbiter is equipped with twelve instruments which are used for optical and microwave remote sensing and to measure fields, particles, and waves (for example magnetic fields, cosmic dust, and plasma waves). The ones most relevant for determination of atmospheric compositions and cloud observations are described here.\textsuperscript{28} The Composite Infrared Spectrometer (CIRS) measures infrared radiation, and therefore temperature and chemical composition, for example of surface features and the atmosphere. The Imaging Science Subsystem (ISS) consists of narrow and wide-angle cameras capturing two-dimensional images between the near-ultraviolet and near-infrared. The Visible and Infrared Mapping Spectrometer (VIMS) measures visible and infrared wavelengths between 0.5-5.1 µm and is one of the most important instruments for long-term observations of clouds. The Cassini Radar (RADAR) uses microwaves for surface imaging, as microwaves have the ability to penetrate through atmospheres, even through a dense and haze-covered one like Titan’s.

The Huygens probe was the first probe to land on a celestial body in the outer solar system. The probe carried six instruments to determine the physical and chemical properties of Titan’s atmosphere and to obtain images of Titan’s surface.\textsuperscript{79} The Huygens Atmospheric Structure Instrument (HASI) measured several physical properties of the atmosphere during the descent, including density, pressure, and temperature. A Gas Chromatograph and Mass Spectrometer (GCMS) measured the atmospheric composition and determined the isotope ratio of the major gaseous components from about 150 km altitude to the surface.\textsuperscript{1} The GCMS also analyzed gas samples from the Aerosol Collector and Pyrolyser (ACP) and investigated the composition of surface materials. The ACP collected a first sample from the lower stratosphere to the tropopause (\(\sim 130-35\) km) and a second sample in the expected cloud layer from \(\sim 25-20\) km.\textsuperscript{80} Other instruments included the Doppler Wind Experiment (DWE), the Descent
Imager/Spectral Radiometer (DISR), and Surface Science Package (SSP), which measured wind speeds, determined the radiation balance and optical properties of aerosols, gathered images in the visible and infrared, and determined surface properties after the landing.

1.3.2 Atmospheric Models

To understand and interpret the data obtained from the Cassini orbiter and the Huygens probe atmospheric models have been developed. Many atmospheric properties are strongly coupled, such as thermal structure, radiative transfer, dynamics, microphysics and photochemistry. These properties were initially addressed separately in photochemical, microphysical, and atmospheric circulation models that incorporate Titan’s physical atmospheric properties. With further advancement of the models, coupling of photochemistry, microphysics and atmospheric circulation has improved and has been combined within general circulation models (GCM) which simulate Titan’s atmosphere.

Photochemical models aim to reproduce the formation of Titan’s haze and atmospheric constituents as well as their vertical atmospheric distributions by simulating gas-phase chemical pathways. One of the first extensive photochemical models for Titan was developed by Yung et al.

Cloud formation and properties are modeled using microphysical models and serve the understanding of how and if clouds are formed, under what conditions (for example at what methane surface relative humidity), at what altitudes, what their composition is, and if precipitation can reach the surface.

The occurrence and distribution of clouds on Titan is one of the most discussed aspects of GCMs which often include simplified microphysical models. Several GCMs for Titan have been developed in the past decade. The further advanced they are the more complex the models become, for example by incorporating the photochemical haze production or by considering seasonal changes in the stratospheric haze distribution. An overview and comparison of several GCMs for Titan is given by Lebonnois et al.

Most models use a series of input parameters that were either obtained from observations or laboratory measurements. These input parameters include Titan’s atmospheric properties such as temperature, pressure and atmospheric abundances as obtained from Cassini and the...
Huygens probe, specific properties of the cloud forming species, such as latent heat, surface energies, and vapor pressures, or in the case of photochemical models experimentally-determined photodissociation and reaction rate constants.\textsuperscript{88,94}

1.3.3 Laboratory Measurements

Laboratory measurements are of great importance for understanding the chemistry of planetary atmospheres. In the case of Titan, gas-phase reactions play a major role in the formation and growth of hydrocarbons and haze. Photochemical models use experimentally-determined reaction rate constants that often need to be extrapolated to lower temperatures.\textsuperscript{93} The chemical dynamics and kinetics of gas-phase reactions at low temperatures that involve ions, radicals and neutral molecules are therefore of major interest, not only for Titan but also for other planetary and interstellar environments, and are readily studied.\textsuperscript{95–97} In addition to gas-phase photochemistry and gas-phase reactions, the irradiation of interstellar ice, and in the case of Titan, ice that potentially forms particles and ice clouds in Titan’s atmosphere, are also studied.\textsuperscript{98,99} From the ice irradiation rate constants, reaction products and the role of surface reactions are determined.\textsuperscript{100}

In the case of Titan’s haze, not only the formation of haze particles but also their optical properties, which depend on composition, particle size and shape, and complex refractive index, are of great interest.\textsuperscript{101,102} The irradiation of cosmically-relevant gases results in residues called “tholins”, which were first described by Sagan and Khare.\textsuperscript{103} This term is also used for Titan analogues produced by the irradiation of methane-nitrogen gas mixtures in laboratory experiments simulating Titan conditions.\textsuperscript{104–107} The latest overview of laboratory investigations of tholins has been given by Cable et al.\textsuperscript{27} Knowledge of haze particle properties is of importance for Titan’s atmospheric models and the calculation of Titan’s radiation balance. Tholins also play a role in the study of cloud formation as they can act as heterogeneous CCN and initiate the condensation of methane and other hydrocarbons in the lower atmosphere. How readily methane, ethane and butane condense onto tholins was studied by Curtis et al.\textsuperscript{108,109}

Experimental investigations on the clouds that form in the lower stratosphere and in the troposphere of Titan have so far been limited to a handful of experiments using a collisional cooling cell in which methane and ethane particles were produced and studied \textit{in situ} us-
ing Fourier transform infrared spectroscopy. The formation, size, and composition of Titan’s cloud condensates are still poorly understood and further laboratory and theoretical investigations are needed.

1.4 Condensable Hydrocarbons in Titan’s Atmosphere

This section discusses the hydrocarbon clouds that can form in Titan’s lower atmosphere (see the “cloud layers” labeled in Fig. 1.1, left-hand panel), and what was known about these clouds at the beginning of this research project in 2009. These clouds, and hydrocarbon aerosols in general, are the focus of the work presented in this thesis. Of major interest are methane, which is ubiquitous in Titan’s atmosphere, and ethane, the major photochemical product of Titan’s photochemistry. Evidence has been found that both of these substances form clouds on Titan.  

1.4.1 Atmospheric Abundances of Hydrocarbons

Atmospheric abundances of gaseous species in Titan’s lower atmosphere from ∼150 km to the surface were determined in situ with the GCMS on-board the Huygens probe. The GCMS also detected evaporating surface constituents after the landing. Titan’s atmosphere consists of ∼95 to 98% nitrogen gas with 1.48 to 5.65% methane gas, depending on altitude, and has a large variety of organic trace species mainly formed from methane photochemistry. Ethane is Titan’s major photochemical product. However, other hydrocarbons are also likely to form, such as propane (C₃H₈), butane (C₄H₁₀), and pentane (C₅H₁₂).

The stratospheric mole fractions of the detected hydrocarbons CH₄, C₂H₆, C₂H₂, and C₃H₈, which are of interest in this thesis, are 0.0148 (0.0565 at surface), 7.9 × 10⁻⁶, 3.2 × 10⁻⁶, and 5.2 × 10⁻⁷, respectively. The mole fractions are averaged over a set of latitudes (70°S, 50°S, 33°S, 15°S, 5°N, 33°N, 50°N, 70°N) since for most species their abundance increases towards the winter polar region.

Other hydrocarbons of interest are butane and pentane. Butane has so far not been detected in Titan’s atmosphere but was estimated to be present at a concentration of ∼200 ppbv using a photochemical model and was furthermore found to be a major product of the irradiation of pure methane and ethane ices. Pentane has so far only been found in corona-
discharge experiments\textsuperscript{[119]} and should be condensable if it is present in sufficient amounts in Titan’s atmosphere.

1.4.2 Titan’s Methane and Ethane Clouds

Evidence has been found for the existence of methane and ethane clouds on Titan. They have been observed at altitudes of around 8-30 km and 30-60 km, respectively.\textsuperscript{[22,77,82,114]}

Ground-based spectroscopic methods and results from the Cassini ISS and VIMS led to the detection of transient, convective methane clouds in the south polar region at altitudes between 15-30 km, driven by solar heating,\textsuperscript{[26,67,76,78,120,121]} and to sporadic mid-latitude clouds which are geographically-driven, for example by cryovolcanic activity.\textsuperscript{[122]} The radii of the cloud particles were estimated to be between 5 $\mu$m and 50 $\mu$m.\textsuperscript{[92,123]}

In addition to the methane clouds in the southern hemisphere evidence for an ethane cloud in the north polar region was found.\textsuperscript{[114]} This ethane cloud appears to be a permanent feature at altitudes between 30-50 km. The cloud is caused by Titan’s atmospheric circulation, which leads to enrichment, subsidence and finally condensation of hydrocarbons above the tropopause in the winter polar region.\textsuperscript{[92,114,124]} Ethane particle sizes were found to be smaller than 3 $\mu$m, much smaller than the southern methane cloud particles, and they are assumed to be solid.\textsuperscript{[114,125]}

A classification of Titan’s clouds can be found in Rannou et al., which provides information on cloud types, location and origin, optical thickness, droplet radius, lifetime, and observations.\textsuperscript{[92]}

1.4.2.1 Potential Importance of Supercooled Liquid Particles

The existence of tropospheric methane clouds was supported by an increase of the methane concentration at an altitude of $\sim$ 16 km and by the detection of an optically thin methane haze at $\sim$ 21 km measured during the descent of the Huygens probe using the on-board GCMS and DISR, respectively.\textsuperscript{[22,115]} Based on the measured temperature, pressure, and methane concentration Tokano et al. analyzed the tropospheric methane relative humidity and proposed a layered cloud structure for Titan.\textsuperscript{[22]}

This layered cloud structure included methane ice clouds at altitudes of 20-30 km, liquid
methane-nitrogen clouds between $\sim 8$-$16$ km, and a cloud gap in between. The gap was explained by the atmospheric region between 16-20 km being too cold for liquid cloud droplets to exist and too dry for methane to condense. Though Tokano et al. considered supercooled liquid CH$_4$-N$_2$ droplets their existence was excluded. The phase of the cloud particles is based on the ambient temperature and the melting point of methane and methane-nitrogen mixtures. This also applies to other cloud models such as those presented by Barth and Toon and Graves et al.\textsuperscript{91,126}

If the phase is based on the ambient temperature then the possibility of supercooled cloud droplets, as are found for water in the Earth’s atmosphere, is left out.\textsuperscript{82,127} Barth and Toon called for laboratory investigations to determine if methane and ethane can form supercooled liquid droplets in Titan’s atmosphere.\textsuperscript{82} The phase of cloud particles is of great importance since it influences particle properties, such as refractive index and particle size, and thus affects Titan’s radiation budget.

The layered cloud structure as proposed by Tokano et al. was confirmed in laboratory studies by Wang et al.\textsuperscript{113} Wang et al. studied methane clouds using a cooling cell under conditions mimicking Titan’s atmosphere from 13-19 km. They found solid methane clouds above $\sim 19$ km and liquid methane-nitrogen clouds below $\sim 16$ km. In addition, they found a cloud gap between 16-19 km in the case of a high concentration of ice nuclei (IN)\textsuperscript{iii} representing a “dirty” atmosphere, and a supercooled methane-nitrogen cloud in the case of a low IN concentration representing a “clean” atmosphere. Since the concentration of haze particles in the troposphere is not well known and therefore the availability of IN might be small, supercooled methane-nitrogen clouds might exist in Titan’s atmosphere.\textsuperscript{92,128}

In the case of the north polar ethane cloud the particles are assumed to be solid.\textsuperscript{114} Barth and Toon studied the evolution of ethane clouds between 8-50 km using a microphysical model and assumed that ethane forms ice clouds in this atmospheric region.\textsuperscript{125} This assumption implies that the phase of the ethane cloud particles was based on the atmospheric temperature between 8-50 km which lies below the melting point of ethane ($T_{fus} = 90.35$ K).\textsuperscript{1129}

The first laboratory investigations of supercooled ethane droplets have been presented by

\textsuperscript{iii}An ice-nucleus is defined as a particle that acts as nucleus for the freezing of a supercooled droplet.
Sigurbjörnsson and Signorell which have shown that ethane can form supercooled liquid droplets under conditions relevant to Titan ($T = 78$ K, $N_2$ atmosphere), which, in the absence of ice-nuclei (IN), are relatively long-lived.\textsuperscript{111}

Methane gas is ubiquitous in Titan’s atmosphere. However, the effect of methane gas on the existence and lifetime of the supercooled ethane droplets has so far not been studied. As ethane aerosols are assumed to act as cloud condensation nuclei (CCN) for methane,\textsuperscript{82} the existence and lifetime of supercooled ethane droplets is of great importance for the nucleation of methane in Titan’s atmosphere and for Titan’s radiation budget; the efficiency of methane nucleation and condensation depends on numerous factors, including solubility and phase of the CCN. Therefore, some questions that are addressed in this thesis are:

- Does the presence of methane gas influence the phase behavior and lifetime of supercooled ethane aerosol droplets and if so, does the effect depend on the methane partial pressure?

- Do methane and ethane form mixed liquid droplets at 78 K and if so, what is the composition of these droplets?

1.4.2.2 Potential Importance of Heterogeneous Freezing

The lifetime of the supercooled phase depends on the degree of supercooling, the droplet size, the droplet composition and the presence of IN. Therefore, the two major processes of interest in the study of the phase behavior of hydrocarbon aerosols are the homogeneous and heterogeneous freezing of supercooled liquid droplets. In the case of heterogeneous freezing, the freezing mechanism, such as immersion or contact freezing, and the type of nuclei, are also of interest. The possible freezing mechanisms and the influence of the nuclei type will be explained shortly.

Cloud microphysical models generally assume that cloud formation on Titan is controlled heterogeneously, by condensation of methane and ethane on bare or hydrocarbon-coated haze particles.\textsuperscript{26,82} The phase of the coating and the condensed methane and ethane were assumed to be based on the temperature, thus the phase is solid at temperatures below, and liquid at temperatures above, the melting point of the pure or mixed particle.\textsuperscript{22,82} Despite the assumption that clouds are formed heterogeneously, homogeneous nucleation cannot be completely ruled
out, since, as mentioned earlier, the concentration of haze particles and especially of CCN and IN in the lower atmosphere is not well known. Therefore both the homogeneous and heterogeneous lifetimes of the supercooled phase should be considered.

According to classical nucleation theory, homogeneous nucleation of the ice phase from the supercooled liquid phase occurs when an ice-embryo is formed within the liquid phase and this ice-embryo exceeds a critical size, $r_{\text{crit}}$, thus overcoming the barrier for nucleation, which arises from the competition between the surface and volume free energies, $\Delta G_S$ and $\Delta G_V$, respectively.\textsuperscript{130} Eq. 1.1 and 1.2 describe the Gibbs free energy of formation, $\Delta G$, of an ice-embryo with radius $r$.\textsuperscript{130,131}

\begin{align}
\Delta G &= \Delta G_S + \Delta G_V \\
\Delta G &= 4\pi r^2 \sigma_{l,i} + \frac{4}{3}\pi r^3 \Delta G_\nu
\end{align}

where $\sigma_{l,i}$ is the surface tension at the liquid-ice interface and $\Delta G_\nu$ is the free energy change of transformation per unit volume.

The maximum free energy of formation, $\Delta G_{\text{crit}}$, is the energy barrier for nucleation found at $r = r_{\text{crit}}$. If the ice-embryo grows beyond $r_{\text{crit}}$, the volume free energy change exceeds the surface free energy change, and the embryo spontaneously grows as demonstrated in Fig. 1.2. $\Delta G_{\text{crit}}$ and $r_{\text{crit}}$ can be derived from $d\Delta G/dr = 0$ which results in

\begin{align}
\Delta G_{\text{crit}} &= \frac{16\pi \sigma_{l,i}^3}{3(\Delta G_\nu)^2} = \frac{4}{3}\pi \sigma_{l,i} r_{\text{crit}}^2
\end{align}

$\Delta G_\nu$ can be expressed either in terms of the supersaturation $S$, which is the ratio of the saturation vapor pressure over the liquid phase ($p_{s,l}$) to the saturation vapor pressure over the ice phase ($p_{s,i}$) at temperature $T$, or in terms of the supercooling $\Delta T$, the difference between the melting point of the droplet, $T_{fus}$, and the ambient temperature $T$, as shown in Eqs. 1.5

\textsuperscript{iv}An ice-embryo is a cluster of molecules in the ice phase.
Figure 1.2: The energy of embryo formation $\Delta G$ as a function of embryo radius $r$. For $r > r_{\text{crit}}$ spontaneous growth of the embryo occurs.

and 1.6, respectively.$^{132}$

$$\Delta G_{\nu} = -k_B T \ln S$$

(1.5)$$

$$\Delta G_{\nu} = -\frac{\Delta H_{\text{fus}} \Delta T}{T_{\text{fus}}}$$

(1.6)

where $k_B$ is the Boltzmann constant, $\Delta H_{\text{fus}}$ is the heat of fusion, and $\nu$ is the molecular volume.

The nucleation rate constant $J$ can be expressed using:

$$J = A \cdot \exp \left[ -\frac{\Delta G_{\text{crit}}}{k_B T} \right]$$

(1.7)

From Eqs. 1.4 and 1.6 it can be seen that $\Delta G_{\text{crit}}$ is proportional to $(\Delta T)^{-2}$, and thus the nucleation rate constant $J$ increases with an increasing degree of supercooling.

Eq. 1.1 to 1.6 also apply to heterogeneous nucleation of the ice phase initiated by an IN. In the case of heterogeneous nucleation the presence of a foreign surface usually lowers the energy barrier for nucleation. The extent to which the IN lowers $\Delta G_{\text{crit}}$ depends on the IN size and IN-substrate interactions which are described by the contact angle between the IN and the substrate.$^{130,131}$ The heterogeneous barrier to nucleation, $\Delta G_{\text{crit}}^{\text{het}}$, is often expressed in terms of the homogeneous barrier to nucleation, $\Delta G_{\text{crit}}$, as presented in Eq. 1.8, where the

Note: $\Delta H_{\text{fus}}$ is defined as the amount of heat required to convert a unit mass of a solid at its melting point into a liquid.
The factor $f$ contains information on the contact angle and IN size.\textsuperscript{130}

\[
\Delta G_{\text{crit}}^{\text{het}} = \Delta G_{\text{crit}} \cdot f
\]  

(1.8)

There are four major mechanisms for the heterogeneous nucleation of the ice phase by an IN:\textsuperscript{130} (i) Deposition nucleation is the direct formation of the ice phase from the vapor phase on the surface of an IN. (ii) Immersion freezing nucleation occurs when the IN is immersed into the liquid phase and initiates freezing once the temperature is low enough. (iii) Condensation freezing describes freezing initiated by an IN almost immediately after condensation of the liquid phase. (iv) Contact freezing occurs when an IN initiates freezing upon contact with a supercooled droplet.

The efficiency of an IN to initiate heterogeneous freezing depends on a number of factors such as IN size, molecular interactions between IN and the substrate, and the number of active sites.\textsuperscript{vi,130} However, these properties can be difficult to quantify and large uncertainties and discrepancies exist.

In Titan’s atmosphere bare and coated haze particles are assumed to serve as CCN and IN for hydrocarbons in the lower stratosphere and troposphere of Titan. Species that can potentially condense and coat haze particles include, for example, C$_2$H$_2$, CO$_2$ and H$_2$O.\textsuperscript{33,133} Sigurbjörnsson and Signorell and Wang et al. have shown that the presence of C$_2$H$_2$ accelerates the freezing of pure supercooled ethane droplets.\textsuperscript{111,134} Different aerosol preparation schemes were used to prepare mixed C$_2$H$_6$/C$_2$H$_2$ particles with different structures, for example a core-shell structure or a particle with multiple regions of pure C$_2$H$_6$ and pure C$_2$H$_2$. However, no systematic studies of heterogeneous nucleation were performed nor were different nucleation mechanisms considered.

The study of heterogeneous nucleation is of importance for gaining insights into the lifetime of supercooled droplets, which in turn is of importance for the nucleation of methane, ethane and other hydrocarbons in Titan’s atmosphere and for Titan’s radiation budget. Here the following research questions are focused upon:

\textsuperscript{vi}Active sites are defined as morphological, chemical, or electrical inhomogeneities on the IN surface that promote nucleation (of condensation or crystallization).\textsuperscript{130}
• How does the presence of trace aerosols affect the lifetime of supercooled liquid ethane aerosol droplets and the phase of other hydrocarbon aerosols?

• How does the nucleation efficiency vary with nuclei composition (C$_2$H$_2$ vs. CO$_2$ vs. H$_2$O)?

• How do different freezing mechanisms influence the crystallization rate of supercooled ethane droplets and of other hydrocarbon aerosols?

1.4.3 The Role of Other Potential Condensates

Methane and ethane are not the only condensates that can form in Titan’s atmosphere. Especially in the north polar region, where the concentration of many atmospheric species is increased and the atmospheric temperature decreased during the winter compared to the equatorial and south polar regions, other condensates can form.

These condensates include, for example, C$_2$H$_2$, C$_3$H$_8$, HCN and C$_2$H$_4$ and are thought to act as CCN and IN for methane and ethane while descending through Titan’s lower stratosphere and troposphere. In this thesis the focus is on short-chained n-alkanes while the HCN and C$_2$H$_4$ aerosols are not considered.

1.4.3.1 Coating of Tholins

Hydrocarbons such as C$_2$H$_2$ and C$_3$H$_8$ are expected to condense around 62 km, above the altitudes where ethane and methane condense. It is assumed that these hydrocarbons condense on and coat haze particles. This is one of the reasons that here the phase behavior of hydrocarbons is studied and not that of the tholin particles themselves. Hydrocarbon-coated haze particles are likely to be better CCN for methane and ethane than bare haze particles. The nucleation of butane onto tholin particles has been investigated in laboratory studies by Curtis et al. who found that, with a required supersaturation of > 1.3, the nucleation of butane onto tholins is rather difficult. The nucleation was studied at a temperature of 125 K, at which n-C$_4$H$_{10}$ forms a disordered solid.

Supersaturation is defined as the ratio of the vapor pressure of a substance to its saturation vapor pressure.
The condensation of hydrocarbons on haze particles alters their surface properties and thus affects the nucleation efficiency of methane and ethane at lower altitudes. How they alter surface properties and affect the nucleation efficiency, however, depends on the phase of the hydrocarbons; thus the overall particle composition is linked to the phase and composition of the hydrocarbon coating. Therefore, the study of the phase behavior of hydrocarbons such as C$_3$H$_8$, C$_4$H$_{10}$, and C$_5$H$_{12}$ under conditions mimicking Titan’s atmosphere, is of great importance and part of the studies presented in this thesis. Specifically, under conditions mimicking Titan’s atmosphere ($T = 78$ K, N$_2$ atmosphere), the following points are of interest:

- the homogeneous and heterogeneous phase behavior of propane aerosol particles

- the homogeneous and heterogeneous phase behavior and the nucleation kinetics of $n$-butane and $n$-pentane aerosol particles

- do propane, $n$-butane, or $n$-pentane form supercooled liquid droplets as has been observed for ethane?

1.4.4 The Potential Role of Lakes

The cloud composition might have important implications for the composition of hydrocarbon lakes, which are mostly found in the north polar region, and vice versa.$^{137-139}$ Brown et al. and Tokano showed that there might be a connection between the lakes and the formation of clouds in the polar regions and that the lake composition (methane-rich or ethane-rich) affects polar meteorology and thus cloud formation in the polar troposphere.$^{139,140}$

According to Tokano’s GCM model the polar meteorology is influenced by the evaporation of methane which depends on the lake composition.$^{140}$ During the northern hemisphere summer, no methane evaporates in the case of ethane-rich lakes. This results in a higher surface temperature of the lakes compared to the land which leads to moist winds from land to sea and hence to enhanced precipitation. In the case of methane-rich lakes evaporation of methane leads to cooling of the lake surface. As a result, the methane partial pressure near the surface eventually exceeds the methane saturation pressure over the lake and evaporation stops. In the case of methane-rich lakes precipitation is scarce due to transport of methane away from
the lakes. Although the model predicts a dependence of the polar meteorology on the lake composition, it fails to reproduce the north polar methane clouds that were observed during the northern hemisphere winter.\cite{Cordier2013}

According to Cordier et al., Titan’s lakes consist of 76-79\% $\text{C}_2\text{H}_6$, 7-8\% $\text{C}_3\text{H}_8$, 5-10\% $\text{CH}_4$ and various solutes, including butane, acetylene and carbon dioxide.\cite{Cordier2012} However, the predicted composition is highly sensitive to the thermodynamic data used in the model and therefore large uncertainties exist.\cite{Drossart2012} Knowledge of the lake composition may offer valuable clues to the major components of rain droplets that reach Titan’s surface, and vice versa. If, for example, rain is the source of Titan’s hydrocarbon lakes, then the composition of the rain droplets must be similar of that of the lakes, and thus be a mixture of $\text{CH}_4$, $\text{C}_2\text{H}_6$, and $\text{C}_3\text{H}_8$.

### 1.5 Thesis Outlook

This thesis presents studies of the phase behavior the aerosols of ethane, propane, $n$-butane and $n$-pentane carried out using Fourier transform infrared spectroscopy. Homogeneous and heterogeneous phase behaviors are studied, the latter in the presence of aerosols of acetylene, carbon dioxide, and water.

Chapter 2 briefly presents the experimental set-up, sample preparation, and data acquisition methods for the study of aerosols and thin films of the hydrocarbons mentioned above.

Chapter 3 discusses the homogeneous and heterogeneous crystallization of supercooled ethane aerosol droplets performed under conditions representative of those in Titan’s lower atmosphere ($\text{N}_2$-$\text{CH}_4$ atmosphere) and the crucial influence of $\text{CH}_4$ gas on the crystallization process. A detailed overview of the IR spectroscopic signatures of pure $\text{C}_2\text{H}_6$ and mixed $\text{C}_2\text{H}_6/\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_6/\text{CO}_2$ aerosols and their phase dependence is provided. The ice-nucleating efficiencies of $\text{C}_2\text{H}_2$ and $\text{CO}_2$ aerosols are compared and the first laboratory experiment comparing the efficiencies of immersion and contact freezing for Titan aerosols is described. The spectral data provided are of use for remote sensing applications, while the nucleation studies have important consequences for models of Titan’s ethane clouds.

Chapter 4 is concerned with the phase behavior of $\text{C}_3\text{H}_8$ and $n$-$\text{C}_5\text{H}_{12}$ aerosol particles. As in Chapter 3, homogeneous and heterogeneous crystallization are studied and $\text{C}_2\text{H}_2$, $\text{CO}_2$, 

...
or $\text{H}_2\text{O}$ aerosols are used as crystallization nuclei. In this chapter a Mie model is applied to obtain a time-dependent particle size distribution that can be used in conjunction with a non-linear fit to obtain the surface and volume nucleation rate constants for $n$-C$_5$H$_{12}$ aerosol particles in a nitrogen atmosphere.

Chapter 5 describes studies of the phase behavior of $n$-C$_4$H$_{10}$ as a thin film between 20 and 140 K and as aerosol particles at 78 K. The results from the thin films studies are used to identify the phases observed in the aerosols, providing a complementary method for the determination of the phase of the aerosol particles. The volume and surface nucleation rate constants for the observed phase transitions of $n$-C$_4$H$_{10}$ aerosol particles are determined using the same method as described in Chapter 4.

Chapter 6 gives an overview of the hydrocarbon aerosols studied in this thesis and other aerosols studied by Signorell and co-workers to provide reference data for astronomical remote sensing. The data can be accessed online (www.vub.ac.be/STER/JAD/jad.htm).

Finally, infrared measurements of thin films of the previously studied hydrocarbons (C$_2$H$_6$, C$_3$H$_8$, n-C$_5$H$_{12}$) are presented. In Chapter 7 thin film measurements used to identify the phases observed in the aerosol measurements carried out between 20 K and the respective melting points are discussed. The obtained IR spectra are compared to literature data and phases that are not observed in the aerosol measurements provide additional reference data for remote sensing applications.
Chapter 2

Experimental

2.1 Infrared Measurements of Hydrocarbon Aerosols

Pure and multicomponent aerosol particle ensembles were generated in a custom built cooling cell by injection of warm \((T = 293 \text{ K})\) sample gas mixtures into a cold \((T = 78 \text{ K})\) bath gas. Rapid cooling of the injected sample led to supersaturation of the gas of interest and eventually to aerosol particle formation. Time-dependent infrared (IR) extinction spectra of unsupported aerosol particles in thermal equilibrium with the surroundings were recorded \textit{in situ} in the cell. This set-up allows the study of intrinsic particle properties, such as phase, size, and architecture, and their change over time. The instrumental set-up, mainly consisting of a custom made cooling cell and a rapid-scan Fourier transform infrared (FTIR) spectrometer, is schematically shown in Figure 2.1. A detailed description is given in the following sections.

2.1.1 Cooling Cell

The bath gas in the cooling cell is cooled to 78 K using liquid nitrogen (LN2) as the coolant. The temperature, pressure and gas-phase composition in the cooling cell can be controlled, and hence it is possible to simulate the conditions present in a wide range of planetary and lunar atmospheres. Here, experimental conditions were chosen to simulate Titan’s lower atmosphere.\textsuperscript{138,115} Heaters are employed to access temperatures above the coolant boiling point. Pressures can be adjusted from 0-1500 mbar. The mid infrared (mid-IR) light beam provided by a globar light source enters the cooling cell via transfer optics. The light makes multiple
Figure 2.1: Sketch of the experimental set-up to study aerosol ensembles, consisting of a FTIR spectrometer and a custom made cooling cell.

passes through the cell (4 to 32 passes, adjustable in increments of 4) by reflection on a set of White optics, resulting in a path length of up to several meters (≈ 0.7-12 m), before it reaches the LN2 cooled mercury-cadmium-telluride (MCT) detector (InfraRed Associates). The path length is chosen depending on the sample concentration and the IR band strength of interest to maximize sensitivity and signal-to-noise ratio. Therefore, for lower concentrations a longer path length is used. The optical path length, however, differs due to reflection, scattering, and absorption losses by windows, mirrors and bath gas. The optical path length can be calibrated using nitrous oxide (N₂O). Details of the optical path length calibration can be found in Appendix A. The cooling cell has an approximate volume of 11 L. Typical mixing ratios of the sample gas in the cooling cell for the measurements here were 10⁻⁵ – 10⁻⁶ and a path length of 12-24 passes was employed. The geometrical path length between the top and bottom mirrors of the cell is 62.5 cm/pass.

2.1.2 Sample Preparation

All sample gas mixtures were prepared in stainless steel bottles as a dilution of 0.5-1.5% of the gas of interest in helium (He) or nitrogen (N₂), depending on the bath gas in the cell. If lower
concentrations were needed the sample was further diluted prior to use. The gases used in this study are summarized in Table 2.1 including their melting point ($T_{fus}$), triple point ($T_{triple}$), and boiling point ($T_{boil}$) temperatures.

All gases were purchased from Praxair, Inc. The methane (CH$_4$) gas was of purity > 99.999%, the ethane (C$_2$H$_6$), propane (C$_3$H$_8$), and carbon dioxide (CO$_2$) gases were of purity > 99.99%, and $n$-butane (n-C$_4$H$_{10}$) gas was of purity > 99.98%. All gases were used as supplied. The bath gases helium (He) (99.999%) and nitrogen (N$_2$) (99.999%) were further purified by freezing out water (H$_2$O) and CO$_2$. Acetylene (C$_2$H$_2$) gas was supplied with a purity of 99.6% and was further purified by freezing out the stabilizer prior to use. The liquids $n$-pentane (n-C$_5$H$_{12}$) (Fisher Scientific, Spectranalyzed) and H$_2$O (UltraPure Water, Cayman Chemical) were used without any further purification. To prepare gas mixtures from these liquids they were placed into a glass tube attached to the gas mixing system. No heating of the liquids was necessary since both have an appreciable vapor pressure at room temperature.

### Table 2.1: Overview of hydrocarbons of interest

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_{fus}$ (K)</th>
<th>$T_{triple}$ (K)</th>
<th>$P_{triple}$ (bar)</th>
<th>$T_{boil}$ (K)</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>90.69$^{[a]}$</td>
<td>90.68$^{[b]}$</td>
<td>0.117$^{[b]}$</td>
<td>111.67$^{[a]}$</td>
<td>3 6</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>90.37$^{[c]}$</td>
<td>90.35$^{[d]}$</td>
<td>1.13 x $10^{-5}$$^{[b]}$</td>
<td>184.55$^{[a]}$</td>
<td>3 6 7</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>85.5$^{[e]}$</td>
<td>85.52$^{[e]}$</td>
<td>1.69 x $10^{-9}$$^{[b]}$</td>
<td>231.14$^{[a]}$</td>
<td>4.3.1 6 7</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>134.87$^{[f]}$</td>
<td>134.86$^{[b]}$</td>
<td>6.74 x $10^{-6}$$^{[b]}$</td>
<td>272.66$^{[f]}$</td>
<td>5 6</td>
</tr>
<tr>
<td>n-C$<em>5$H$</em>{12}$</td>
<td>143.4$^{[g]}$</td>
<td>143.48$^{[b]}$</td>
<td>7.7 x $10^{-7}$$^{[b]}$</td>
<td>309.21$^{[a]}$</td>
<td>4.3.2 6 7</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>188.45$^{[a]}$</td>
<td>192.4</td>
<td>1.26</td>
<td></td>
<td>3 4 5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>194.69$^{[a]}$</td>
<td>216.59</td>
<td>5.180</td>
<td></td>
<td>3 4 5</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>273.15</td>
<td>273.16</td>
<td>0.0061</td>
<td>373.12</td>
<td>4 5</td>
</tr>
</tbody>
</table>

$^{[a]}$Lide$^{21}$, $^{[b]}$Younglove and Ely$^{143}$, $^{[c]}$Klimenko et al.$^{144}$, $^{[d]}$Pavese$^{129}$, $^{[e]}$Pavese and Besley$^{145}$, $^{[f]}$Aston and Messerly$^{146}$, $^{[g]}$Wei$^{147}$, $^{[h]}$Ruzicka and Majer$^{148}$

*sublimation point ($T_{sub}$)

### 2.1.3 Injection Methods

To form pure and various mixed aerosol particles different injection methods were used. In our system, two different sample gases can be introduced through separate heated inlet tubes t1 and t2 ($T >$ dew point of the gas of interest) which are operated by two magnetic solenoid valves (Bürkert), valve 1 (v1) and valve 2 (v2) (see Fig. 2.1). The opening times of the valves were typically between 0.5 and 1 s. For the formation of pure hydrocarbon aerosols, only inlet
Figure 2.2: Injection schemes for gas samples: (i) one-component and premixed injection, (ii) sequential injection with a time delay $\Delta t$ between the two pulses.

t1 and valve v1 were used (see Fig. 2.2(i)). This scheme was also employed when premixed gas samples of hydrocarbon with either CO$_2$, C$_2$H$_2$, or H$_2$O were injected into the cell (“premixed injection”).

For “sequential injections” of two different gas samples both inlet tubes were used and a time delay $\Delta t$ between the opening of v1 and the opening of v2 was introduced (see Fig. 2.2(ii)). Typically, $\Delta t$ varied between 500 ms and 6000 ms.

The different injection schemes enabled some control over the degree of internal or external mixing of multicomponent aerosol particle ensembles. For example, with a proper time delay core-shell particles can be formed as demonstrated by Firanescu et al., Signorell and Jetzki, and Signorell et al. This set-up also allows for studying different types of freezing mechanisms such as immersion or contact freezing.

2.1.4 Acquisition of Spectra

A series of individual mid-IR extinction spectra were recorded in transmission using the Bruker IFS 66v/S rapid-scan spectrometer. Its major components are a Michelson interferometer, a helium-neon (HeNe) laser to control the interferometer, a potassium bromide (KBr) beam split-
ter and a silicium carbide (SiC) globar as the mid-IR light source. The resolution and aperture of the FTIR can be adjusted from 0.25 to 12 cm\(^{-1}\) and from 0.25 to 12 mm, respectively. The standard frequency range for the IFS 66v/S is 7500-370 cm\(^{-1}\).

Here, spectra were recorded in the region from 8000 to 500 cm\(^{-1}\) with a spectral resolution of 0.5 cm\(^{-1}\) starting immediately after particle formation with total measurement times ranging from 20 minutes to 2 hours. The time intervals between individual spectra varied between 2 and 300 seconds and the number of scans each spectrum was averaged over varied between 1 and 20. Shorter time intervals and a smaller number of scans were used at early times when the phase of the particles tends to change rapidly, while longer time intervals and a larger number of scans were used at later times in the measurement when spectral changes came to a halt. Longer measurement times could not be realized for conditions that are relevant to Titan because of diffusion of the aerosol particles out of the IR light beam. The recorded IR signals become weaker over time for the same reason. Instrumental settings used for measurements with the IFS 66v/S FTIR spectrometer can be found in Appendix A, Table A.3.

2.1.5 Experimental Conditions and Execution

Prior to aerosol generation, the cooling cell was filled with 550-800 mbar of a bath gas (He or N\(_2\)) and was pre-cooled to a temperature of 78 K (corresponding to the temperature at an altitude of \(\sim\) 18 km and \(\sim\) 60 km in Titan’s atmosphere). Pure or multicomponent aerosol particle ensembles were generated by injecting warm \((T = 293 K)\) sample gases (diluted in He or N\(_2\)) into the pre-cooled bath gas. The backing pressure of the sample gas was typically 1.5 to 3 bar.

For the mixed aerosols, the ratios of C\(_2\)H\(_6\), C\(_3\)H\(_8\), n-C\(_4\)H\(_{10}\) or n-C\(_5\)H\(_{12}\) to CO\(_2\), C\(_2\)H\(_2\), or H\(_2\)O were typically 4:1, 3:1, 2:1 or 1:1. Mixed aerosol experiments are the attempt to simulate the presence of other trace aerosols in Titan’s atmosphere that could serve as heterogeneous condensation and crystallization nuclei for hydrocarbon particles.

In an attempt to obtain the IR spectra of liquid hydrocarbon droplets, their spectra were also recorded above the respective melting points of the bulk by adjusting the cell temperature with the heating unit. More substance specific details for the experimental conditions can be found in each of the Chapters 3-5.
2.2 Infrared Measurements of Hydrocarbon Thin Films

Measurements of thin films were performed in the laboratory of Prof. Dr. Takamasa Momose, at the University of British Columbia. A similar experimental set-up has previously been used for studies of low temperature solids.\textsuperscript{152-154} Thin films of liquid and solid \textit{n}-alkanes from \textit{C}\textsubscript{2}-\textit{C}\textsubscript{5} were prepared and studied between 20 K and the respective melting points using mid-IR spectroscopy. Thin film measurements allow temperatures below 78 K to be accessed under relatively stable temperature conditions and therefore the observation of phases that are not accessible using the cooling cell. The cooling cell can in theory be used with liquid He instead of LN2 to access temperatures below 78 K. However, the cooling cell has a large volume and to control and obtain stable temperatures above the coolant boiling point is much more difficult compared to the thin film measurements.

2.2.1 Instrumental Set-up

The experimental set-up for thin film measurements is shown in Fig. \textsuperscript{2.3}. A sample holder is mounted to a copper platform (cold stage) which is in thermal contact with the second-stage (3.5-4.2 K) of a closed-cycle 2-stage He-cryostat (RDK-205D-0.5W, Sumitomo Heavy Industries Ltd., Japan) that cools the sample holder to \( \sim 4 \) K. The sample holder used was either a zinc-selenium (ZnSe) substrate for vapor-deposited samples, or an enclosed optical cell consisting of a copper housing and two ZnSe optical windows for the liquid samples. The sample holder is surrounded by a copper cold-shield connected to the first-stage (35-50 K) of the He-cryostat. Both, the sample holder and the cryostat head are embedded in a stainless steel vacuum chamber (\( p < 10^{-6} \) mbar). Thermocouples and heating units allow the temperature of the cold stage and the sample holder to be controlled and monitored. During deposition the sample flow is controlled using a mass flow controller (Horiba Stec Sec-4400 Mass Flow Controller MFC 500 sccm). IR absorption spectra are recorded with a FTIR spectrometer (Bruker IFS 125HR) in combination with a MCT detector (MCT-316/2M, InfraRed Associates). The vacuum chamber and optics are separated by KBr windows and separately evacuated using a turbo and a rotary pump, respectively.
2.2.2 Sample Preparation

2.2.2.1 Vapor Deposition

Using the method of vapor deposition, an amorphous thin film of the substance of interest was produced by deposition of undiluted sample gas (except for $\text{C}_3\text{H}_8$ which was a dilution of 3.5% in He) onto a 25 mm in diameter and 5 mm thick ZnSe substrate at 20 K with a flow rate of 10 ccm (sample pathway through valve 1 in Fig. 2.3). The substrate was embedded in the vacuum chamber and deposition took usually only several seconds. The pressure in the vacuum chamber was $< 10^{-6}$ mbar. Usually, the vacuum chamber is continuously pumped during thin film measurements to keep the pressure below $10^{-6}$ mbar for thermal insulation. However, here, the samples were heated close to the melting point. Continuous pumping would lead to an early loss of the sample due to an increasing vapor pressure upon heating. Therefore, the pump was disconnected through a valve from the vacuum chamber and only reconnected if the pressure increased above $10^{-4}$ mbar. After deposition the temperature was gradually increased until evaporation and loss of the sample to colder parts of the system occurred. During a phase transition the temperature was kept constant until completion of the transition or no further change in the spectrum was observed. The stability of the temperature was within $\sim 1$ K.
2.2.2.2 Optical Cell Condensation

To obtain a spectrum of the liquid n-alkane of interest, the undiluted sample gas was injected into an enclosed optical cell at a temperature several °K above its melting point at a flow rate of either 100 or 500 ccm (sample pathway through valve 2 in Fig. 2.3). The sample gas condensed as a liquid film on the walls and windows of the cell. The pressure in the optical cell was unknown since no pressure gauge is connected to it. The pressure of the surrounding vacuum chamber was kept < 10^{-6} mbar for thermal insulation. The enclosed optical cell consisted of a copper housing and two 5 mm thick ZnSe optical windows. The inner diameter and path length of the two optical cells used were 20 (10) and 15 mm (5.25 mm), respectively. Once enough sample in the cell had condensed to obtain a liquid infrared spectrum, the temperature was gradually lowered to 78 K and below to observe crystallization. Afterward, samples were either annealed\textsuperscript{[ii]} at higher temperatures or simply transformed back into the liquid phase.

2.2.3 Acquisition of Spectra

Mid-IR absorption spectra of liquid and solid thin films of n-alkanes from C_{2}-C_{5} were recorded in transmission using the Bruker IFS 125HR spectrometer equipped with a KBr beam splitter and globar as the mid-IR light source. The IFS 125HR spectrometer has a maximum resolution < 0.0063 cm\textsuperscript{-1} and an adjustable aperture from 0.5 to 12.5 mm, respectively. The standard frequency range for the mid-IR region of the IFS 125HR is 4800-620 cm\textsuperscript{-1}.

IR absorption spectra were recorded from 12000-500 cm\textsuperscript{-1} at temperatures ranging from 20 K to several °K above the melting point of each substance with a resolution of 0.5 cm\textsuperscript{-1}. Every spectrum was an average of 20 scans (total scan time \sim 18 s). Instrumental settings for measurements with the IFS 125HR FTIR spectrometer can be found in Appendix A, Table A.4.

\textsuperscript{[ii]}The annealing process is here defined as the exposure of the sample to a constant temperature over minutes to hours resulting in the rearrangement of the solid structure.
Chapter 3

The Influence of Methane, Acetylene and Carbon Dioxide on the Crystallization of Supercooled Ethane Droplets in Titan’s Clouds

3.1 Introduction

In recent decades, Titan has attracted considerable attention owing to its similarities to Earth. With a nitrogen-based atmosphere, an atmospheric pressure at the surface which is more similar to that of the Earth than any other body in the solar system, and a rich photochemistry, Titan is considered to provide the opportunity to study chemical and physical processes in a system similar to the primitive Earth. The landing of the Huygens probe on Titan in 2005 as part of the highly-successful Cassini-Huygens Mission provided the first detailed images of the surface and allowed the determination of the moon’s atmospheric temperature and pressure profile and the atmospheric composition.

Titan’s methane (CH$_4$) cycle appears to be similar to the terrestrial hydrological cycle. CH$_4$ aerosol haze, clouds and precipitation are all known to be present in the atmosphere of Titan. Recent laboratory studies by Signorell and co-workers have revealed the phase behavior of CH$_4$ aerosols relevant to the lower atmosphere of Titan and their potential role in
cloud formation. For example, they confirmed the feasibility of the existence of layered CH$_4$ clouds, as predicted by Tokano et al., and demonstrated that supercooled liquid N$_2$-CH$_4$ cloud droplets can exist between the layers.

The potential importance of ethane (C$_2$H$_6$) aerosols and cloud condensates in Titan’s atmosphere has also been demonstrated. For example, cloud models predict the existence of widespread C$_2$H$_6$ clouds in the polar regions, and Cassini’s visual and infrared mapping spectrometer (VIMS) provided strong evidence for C$_2$H$_6$ clouds in the region of the northern pole.

While the evidence for the existence of C$_2$H$_6$ clouds is convincing, the current understanding of the microphysical properties of such clouds is limited. For example, there is little direct information on the phase of C$_2$H$_6$ cloud particles, and cloud models currently treat the phase of cloud condensates as based solely on the ambient temperature, failing to take into account the freezing kinetics of such particles and the possible occurrence of long-lived supercooled liquid particles. Laboratory studies of C$_2$H$_6$ clouds have been carried out in order to address this deficiency. By monitoring the evolving shape of characteristic IR absorption bands which are sensitive to phase, Sigurbjörnsson and Signorell performed measurements of the freezing kinetics of supercooled C$_2$H$_6$ droplets, providing evidence that such droplets can persist for significant periods of time in the atmosphere of Titan.

Furthering the understanding of C$_2$H$_6$ cloud formation and stability is also necessary for understanding the occurrence and composition of the liquid features present on the surface of Titan. While evidence for the existence of liquid-filled lakes has been found, the composition of these features is not well known, although strong indications of the presence of C$_2$H$_6$ have been found. More information on Titan’s atmospheric composition, cloud observations, and laboratory studies can be found in Chapter 1.

In this chapter, detailed laboratory studies of C$_2$H$_6$ cloud condensates performed under conditions that mimic those present in Titan’s lower atmosphere are presented, describing the influence of CH$_4$ and presence of trace aerosol species such as acetylene (C$_2$H$_2$) and carbon dioxide (CO$_2$) on the stability and crystallization of supercooled C$_2$H$_6$ droplets. As in the previous work by Signorell and co-workers, the temporal evolution of infrared (IR) absorption
spectra is used to elucidate the phase behavior of supercooled $C_2H_6$ aerosols. By carrying out this work it has been possible to:

- provide a detailed overview of the spectroscopic signatures of pure $C_2H_6$, mixed $C_2H_6/C_2H_2$, and mixed $C_2H_6/CO_2$ aerosols for use as a reference in remote sensing applications (Section 3.3.1)

- provide detailed information on the phase-dependence of all relevant IR bands of $C_2H_6$ (Section 3.3.2)

- provide previously unreported information on the IR spectral signature of the metastable phase I solid $C_2H_6$ and the conditions affecting its occurrence (Sections 3.3.2 and 3.3.3)

- quantitatively compare the ice-nucleating effectiveness of $C_2H_2$ and $CO_2$ aerosols for supercooled $C_2H_6$ droplets, and to rationalize the observed difference in terms of the crystal structure of the particles (Section 3.3.3)

- perform the first experimental investigation of the influence of freezing mechanism on the rate of crystallization of supercooled $C_2H_6$ droplets under conditions relevant to the atmosphere of Titan (Section 3.3.4).

### 3.2 Experimental

The experimental set-up and conditions are described in Chapter 2.1. Here the more specific details on the experimental conditions to study the influence of $CH_4$ gas and trace species on the crystallization of supercooled liquid $C_2H_6$ droplets are given. Pure and mixed composition ensembles of $C_2H_6$ particles were studied.

In these measurements the cooling cell was filled with either pure nitrogen ($N_2$) (or helium (He)) or a mixture of $CH_4$ and $N_2$ (or He) gas in order to simulate the lower atmosphere of Titan and pre-cooled to 78 K. The total gas pressure was maintained at $\sim 550$ mbar, matching the atmospheric pressure at an altitude of $\sim 18$ km, while the mole fraction of $CH_4$ gas ($x_{CH_4}$) in the cell was varied from 0 to 0.025, covering the range found in Titan’s atmosphere from the stratosphere down to an altitude of $\sim 18$ km. Under these conditions, $CH_4$ cannot condense
to aerosols, but remains in the gaseous state. $C_2H_6$ aerosols were generated by injecting warm $C_2H_6$ gas diluted in $N_2$ (or He) into the pre-cooled cell. The $C_2H_6$ mole fraction used in this study ($\sim 5 \times 10^{-5}$) was similar to that present in Titan’s stratosphere; values for the lower atmosphere are not currently available. The systematic variation of $y_{CH_4}$ allowed us to demonstrate the influence of gaseous CH$_4$ on the properties of $C_2H_6$ aerosols.

All experiments were repeated in presence of $C_2H_2$ and CO$_2$ ice aerosols, respectively. For mixed composition ensembles the different injection methods, premixed and sequential, were used to mimic immersion and contact freezing. The time delay for sequential measurements was $\Delta t = 1.5-6$ s (valve opening time = 1.0 s). The trace gas ($C_2H_2$ or CO$_2$) concentration used was approximately one third of that of $C_2H_6$. The gases were injected into the cell diluted in the major bath gas. For the pre-mixed injection method the trace gases were also pre-mixed with $C_2H_6$ gas.

Mid infrared (mid-IR) absorption spectra of the aerosol ensembles were recorded in the region from 4000 to 500 cm$^{-1}$. The spectra were recorded with a spectral resolution of 0.5 cm$^{-1}$ at time intervals of between 2 and 200 seconds, starting immediately after particle formation and continuing for a total time of 40 minutes to one hour.

### 3.3 Results and Discussion

#### 3.3.1 Overview of Spectroscopic Signatures of Pure and Mixed Aerosols

In this section a detailed overview of the spectral signatures of pure $C_2H_6$ and mixed $C_2H_6$/$C_2H_2$ and $C_2H_6$/$CO_2$ aerosols is provided. Spectroscopic information on aerosols relevant to Titan is scarce, and hence these data are expected to be of considerable use for remote sensing applications. Fig. 3.1 reports the mid-IR absorption spectra of (A) pure $C_2H_6$ aerosols formed in a $N_2$ atmosphere, (B) $C_2H_6$ aerosols formed in a mixed $N_2/CH_4$ atmosphere ($y_{CH_4} = 0.007$), (C) mixed $C_2H_6$/$C_2H_2$ aerosols formed in a $N_2$ atmosphere, and (D) mixed $C_2H_6$/$CO_2$ aerosols formed in a $N_2$ atmosphere. The spectra were recorded $\sim 1$ s after the injection of pure $C_2H_6$ or the appropriate premixed combination of gases into the cell.

Fig. 3.1A shows the characteristic unstructured bands of pure supercooled $C_2H_6$ droplets, which form after injection of $C_2H_6$ into the cell. The bands at 2976, 2941, and 2881 cm$^{-1}$ are
Figure 3.1: IR spectra of (A) supercooled C$_2$H$_6$ aerosol droplets in N$_2$ gas, (B) supercooled C$_2$H$_6$ aerosol droplets in a N$_2$/CH$_4$ gas mixture with $y_{CH_4} = 0.007$, (C) mixed C$_2$H$_6$/C$_2$H$_2$ aerosols in N$_2$ gas, and (D) mixed C$_2$H$_6$/CO$_2$ aerosols in N$_2$ gas. The spectra were recorded $\sim 1$ s after injection of the sample gases into the cooling cell.

the $\nu_7$ CH-stretching, the $\nu_8 + \nu_{11}$ combination, and the $\nu_5$ CH-stretching bands, respectively, in accordance with the bulk measurements of Tejada and Eggers and Wisnosky et al.\cite{157,158} The weak features observed at 2913 and 2737 cm$^{-1}$ are the $\nu_1$ symmetric CH-stretching and the $\nu_2 + \nu_6$ symmetric CH$_3$-deformation bands, respectively.\cite{100} The three bands observed at 1463, 1370, and 819 cm$^{-1}$ are the $\nu_8$ asymmetric CH$_3$-deformation, $\nu_6$ symmetric CH$_3$-deformation, and $\nu_9$ CH$_3$-rocking fundamentals, respectively.\cite{157,158}

Fig. 3.1B shows a spectrum of pure supercooled C$_2$H$_6$ droplets formed in a N$_2$/CH$_4$ atmosphere ($y_{CH_4} = 0.007$). In contrast to Fig. 3.1A, additional rovibrational transitions of cold CH$_4$ gas are visible in the regions around 3000 cm$^{-1}$, 1500 cm$^{-1}$ and 1300 cm$^{-1}$. The CH$_4$ saturation vapor pressures over the solid and the liquid at 78 K are $\sim 14$ and $\sim 17$ mbar, respectively;\cite{159} the CH$_4$ concentration in the cell does not exceed these values and hence CH$_4$ aerosols are not formed under these conditions.

The IR absorption spectrum of mixed C$_2$H$_6$/C$_2$H$_2$ aerosols is shown in Fig. 3.1C. Owing to the relatively high sublimation point of C$_2$H$_2$ (189 K), solid particles are formed immediately upon injection of C$_2$H$_2$ gas into the cold cell. The solid C$_2$H$_2$ particles act as heterogeneous
condensation nuclei for C\textsubscript{2}H\textsubscript{6}, forming particles consisting of an C\textsubscript{2}H\textsubscript{2} core and an C\textsubscript{2}H\textsubscript{6} shell, and then as ice-nuclei for the crystallization of the condensed C\textsubscript{2}H\textsubscript{6} shell (see Section 3.3.3). Absorption features of solid C\textsubscript{2}H\textsubscript{2} aerosols are observed at 3227 cm\(^{-1}\) (\(\nu_3\), antisymmetric CH-stretching mode with a weak shoulder at 3222 cm\(^{-1}\) arising from \(^{13}\text{C}\) isotopic substitution), 1389 cm\(^{-1}\) (\(\nu_4 + \nu_5\) combination band), and 787, 772, and 762 cm\(^{-1}\) (\(\nu_5\) bending mode). The splitting of the \(\nu_5\) bending mode into three distinguishable peaks is consistent with an orthorhombic crystalline structure of C\textsubscript{2}H\textsubscript{2} \cite{160,161}. In Fig 3.1C some crystallization of C\textsubscript{2}H\textsubscript{6} has occurred and hence features that arise from both liquid C\textsubscript{2}H\textsubscript{6} (broad) and the solid phase (sharp) are visible. A more detailed discussion of the dependence of the C\textsubscript{2}H\textsubscript{6} band shapes on the particle phase is provided in Sections 3.3.2 and 3.3.3.

Finally, Fig. 3.1D shows the spectrum of mixed C\textsubscript{2}H\textsubscript{6}/CO\textsubscript{2} aerosols. CO\textsubscript{2} also has a relatively high sublimation point (195 K), and solid CO\textsubscript{2} particles are formed immediately upon injection of CO\textsubscript{2} gas into the cold cell. The solid CO\textsubscript{2} particles act as heterogeneous condensation nuclei for C\textsubscript{2}H\textsubscript{6} and then as ice-nuclei for the crystallization of the condensed C\textsubscript{2}H\textsubscript{6} (see Section 3.3.3). Besides the characteristic bands of supercooled liquid C\textsubscript{2}H\textsubscript{6}, two strong absorption features of solid CO\textsubscript{2} appear in the spectrum: the \(\nu_3\) antisymmetric stretching mode at 2356 cm\(^{-1}\) and the \(\nu_2\) bending mode, which is split into two peaks which are observed at 665 and 656 cm\(^{-1}\). Splitting of the \(\nu_2\) bending mode is a clear indication that CO\textsubscript{2} is in the cubic crystalline phase. \cite{162,163} The \(\nu_3\) band is usually saturated under the present conditions owing to the high transition dipole moment associated with excitation of the antisymmetric CH-stretching mode, and therefore cannot be used for analysis. The \(\nu_1 + \nu_3\) and \(2\nu_2 + \nu_3\) combination bands of CO\textsubscript{2} were observed at 3708 and 3600 cm\(^{-1}\), respectively, but are not shown. \cite{162}

Sigurbjörnsson and Signorell have previously demonstrated that the shapes of characteristic IR absorption bands can be used to determine the phase of C\textsubscript{2}H\textsubscript{6} aerosol particles. \cite{111} In this previous study the \(\nu_9\) band of C\textsubscript{2}H\textsubscript{6} at 820 cm\(^{-1}\) was used to monitor particle phase changes. Here the spectrum of C\textsubscript{2}H\textsubscript{6} for the extended frequency range from 3300 to 650 cm\(^{-1}\) is reported. This range includes the \(\nu_8\) and \(\nu_6\) fundamental modes which appear at 1465 cm\(^{-1}\) and 1370 cm\(^{-1}\), respectively. In Section 3.3.2 it will be demonstrated that the bands arising
from these modes are also sensitive to phase, and hence phase transitions of C$_2$H$_6$ aerosols can be studied by monitoring their temporal evolution. It should be noted that the bands of C$_2$H$_6$ appearing above 2700 cm$^{-1}$ are insensitive to phase and crystal structure and hence are not useful for elucidating the properties of C$_2$H$_6$ particles. These extensions to the frequency range of the available spectroscopic information for C$_2$H$_6$ aerosols are important for fully exploiting the optical windows available for planetary remote sensing measurements seeking to investigate cloud processes on Titan.

3.3.2 Spectroscopic Studies of the Homogeneous Crystallization of Ethane and the Influence of Methane Gas

Here the homogeneous crystallization of supercooled C$_2$H$_6$ droplets and the influence of CH$_4$ gas is reported. In particular the spectral features of all of the phase-dependent IR bands of C$_2$H$_6$ (the $\nu_9$, $\nu_6$ and $\nu_8$ bands) are described, and information on the occurrence and IR spectral signature of phase I solid C$_2$H$_6$ is provided.

Figs. 3.2, 3.3, and 3.4 show the temporal evolution of the $\nu_9$, $\nu_6$ and $\nu_8$ bands of C$_2$H$_6$ aerosols, respectively, for varying mole fractions of CH$_4$ gas in the cell ($y_{\text{CH}_4} = 0, 0.007$ and 0.015 parts A, B and C, respectively). For Titan’s atmosphere, the results for $y_{\text{CH}_4} = 0.015$ and higher are the most relevant, as there $y_{\text{CH}_4}$ varies between 0.014 and 0.0565 depending on the altitude.\textsuperscript{115} In the absence of CH$_4$ gas (part A), the supercooled C$_2$H$_6$ droplets, which are formed immediately after injection of C$_2$H$_6$ into the cell, are stable for several hundreds of seconds ($t = 1$ and 212 s), as was previously observed by Signorell and co-workers.\textsuperscript{111} Over time ($t = 1252$-2347 s), homogeneous freezing leads to the formation of crystalline particles which give rise to characteristic structured IR bands. Under these conditions, in the absence of CH$_4$ gas, the phase transition from liquid C$_2$H$_6$ droplets to solid particles in the stable monoclinic crystal phase (phase II, $t = 2347$ s) occurs via a short-lived intermediate cubic crystal phase (phase I, $t = 1252$ and 1768 s), as was previously observed by Signorell and co-workers.\textsuperscript{111,164} In the bulk, phase I has been found to be stable only in the narrow temperature range from 89.9 to 90.3 K and thus this phase is metastable under these measurement conditions.\textsuperscript{164,165} The transition into the stable monoclinic phase II is complete at $\sim t = 2347$ s. During the crystallization process the IR bands show features arising from liquid C$_2$H$_6$ and phase I and
Figure 3.2: The temporal evolution (top to bottom) of the \( \nu_9 \) fundamental during homogeneous freezing of supercooled C\(_2\)H\(_6\) droplets formed in (A) pure N\(_2\) gas, (B) a CH\(_4\)/N\(_2\) atmosphere with \( y_{\text{CH}_4} = 0.007 \), and (C) a CH\(_4\)/N\(_2\) atmosphere with \( y_{\text{CH}_4} = 0.015 \). The presence of CH\(_4\) gas decreases the freezing rates.

phase II solid C\(_2\)H\(_6\).

Fig. 3.5 shows the IR absorption spectra of crystalline C\(_2\)H\(_6\) aerosols in phase II and phase I (parts A and B, respectively). The spectrum shown in part B is a difference spectrum produced from a mixed phase I/phase II spectrum and a pure phase II spectrum. Fig. 3.5 clearly demonstrates that the two phases have distinct IR bands. While the \( \nu_9 \) band of phase I C\(_2\)H\(_6\) has previously been reported,\(^{111}\) to the best of our knowledge this is the first report of the spectrum of phase I in the region of the \( \nu_6 \) and \( \nu_8 \) bands. Phase II has four characteristic peaks at 825, 824, 817 and 814 cm\(^{-1}\), a doublet at 1371 and 1368 cm\(^{-1}\) and three peaks at 1466, 1457 and 1451 cm\(^{-1}\).\(^{157,158}\) For phase I, the expected six peaks at 824, 822, 820, 819, 816 and 814 cm\(^{-1}\) are observed,\(^{111}\) as well as two peaks at 1370 and 1365 cm\(^{-1}\) and three peaks at 1470, 1465 and 1458 cm\(^{-1}\). Note that weak signals arising from phase II C\(_2\)H\(_6\) could still be present in the spectrum in part B.

The evolution of the spectral features of pure C\(_2\)H\(_6\) droplets were examined for varying CH\(_4\) gas content in the cooling cell (parts B and C in Figs. 3.2\textendash}3.4). Any one of the \( \nu_9 \), \( \nu_6 \) or \( \nu_8 \) bands of C\(_2\)H\(_6\) aerosols can be used to compare the rate of freezing as the amount of
Figure 3.3: Analogous to Fig. 3.2, but for the $\nu_6$ fundamental. The sharp peaks below 1370 cm$^{-1}$ in parts B and C arise from rovibrational transition of cold CH$_4$ gas (see also Fig. 3.1B). Note that the C$_2$H$_6$ bands reduce in signal over time because of diffusion of the particles out of the IR beam.

Figure 3.4: Analogous to Fig. 3.2, but for the $\nu_8$ fundamental. The additional sharp peaks in parts B and C (not present in part A) arise from rovibrational transitions of cold CH$_4$ gas.
Figure 3.5: IR spectra of crystalline C$_2$H$_6$ aerosol particles: (A) monoclinic phase II, (B) cubic phase I. The slanted baseline of the $\nu_8$ band in part B is due to elastic light scattering by the particles.

CH$_4$ gas is varied. From the figures it can be seen that the presence of CH$_4$ gas delays the crystallization of C$_2$H$_6$, and that the effect is more pronounced for the higher CH$_4$ content; for $y_{CH_4} = 0.007$ (part B), most of the C$_2$H$_6$ particles are liquid at 2347 s, evident from the fact that only weak features of the solid phase are observable, while for $y_{CH_4} = 0.015$ (part C), crystallization is delayed beyond the timescale of the experiment and only the broad IR bands characteristic of liquid C$_2$H$_6$ droplets are observed. The same behavior is observed for $y_{CH_4} > 0.015$; owing to the limited observation time of these measurements it is not possible to determine whether increasing $y_{CH_4}$ beyond 0.015 has any further effect on the crystallization kinetics of C$_2$H$_6$ droplets. Alternative measurement techniques that allow observations on a longer timescale would be required to determine this, and are currently being developed. Owing to the dominance of the spectral features of liquid C$_2$H$_6$ as a result of the slow freezing kinetics, it is not possible to determine if crystallization proceeds via solid phase I C$_2$H$_6$ for homogeneous freezing in the presence of CH$_4$ gas from these measurements.

It was observed that the particle size increases with increasing $y_{CH_4}$, indicated by the increasingly-slanted baselines of the recorded spectra (not shown). Slanting of the baseline.

---

$^1$An example for the slanted baseline can be found in Appendix B, Fig. B.2
results from elastic scattering of light by large particles and is thus an indication of the formation of larger particles at higher $y_{\text{CH}_4}$.

The increase in particle size with increasing $y_{\text{CH}_4}$ and the observed decrease in the droplet freezing rate are consistent with the incorporation of CH$_4$ into the C$_2$H$_6$ droplets. Albeit for a higher temperature, further evidence for CH$_4$ incorporation has been found in theoretical work on CH$_4$/C$_2$H$_6$ mixtures. However, because the IR absorption bands of gas-phase CH$_4$ coincide with those of liquid CH$_4$, direct spectroscopic evidence for the incorporation of CH$_4$ into C$_2$H$_6$ droplets cannot be attained from the present experimental data.

The observed results from Figs. 3.2-3.4 clearly show that the presence of CH$_4$ gas inverts the C$_2$H$_6$ crystallization process. The observed delay of the C$_2$H$_6$ droplet crystallization with an increasing $y_{\text{CH}_4}$ in the gas phase can be explained by considering freezing point depression below that of pure C$_2$H$_6$ droplets that will accompany incorporation of CH$_4$ into the droplets. This shift of the freezing point towards the ambient temperature in the cell reduces the degree of supercooling of the mixed-composition droplets compared with the pure droplets, which consequently reduces the freezing rate. From preliminary experiments analogous to those described in Wang et al., an upper limit on the CH$_4$ content of the droplets $\sim$ 20% is estimated.

Assuming ideal behavior, the freezing point depression, $\Delta T$, can be estimated as a function of the CH$_4$ content from:

$$\Delta T = \left(\frac{RT_{\text{pure}}}{\Delta H_{\text{pure}}}\right) \cdot x$$  \hspace{1cm} (3.1)

where $x$ is the mole fraction of CH$_4$ ($x_{\text{CH}_4}$) in the liquid C$_2$H$_6$ droplets, $T_{\text{pure}}$ = 89.87 K is the melting point of pure C$_2$H$_6$, and $\Delta H_{\text{pure}}$ = 2.857 kJ mol$^{-1}$ is the heat of fusion of pure C$_2$H$_6$.

The calculated freezing points of two C$_2$H$_6$/CH$_4$ mixtures representative of droplet compositions that seem reasonable are provided in Table 3.1, along with the value for pure C$_2$H$_6$.

A quantitative analysis of the influence of gas-phase CH$_4$ on the kinetics of homogeneous crystallization of supercooled C$_2$H$_6$ droplets is unfortunately not possible from these measure-
ments. Only in the case of freezing in the absence of gas-phase CH$_4$ is the phase transition complete within the timescale of the experiment, which is required for the accurate determination of the rate constant for this process.$^{108}$ The volume freezing rate constant of pure liquid C$_2$H$_6$, $J_{ethane}$, at 78 K has previously been determined to be $\sim 10^8$ cm$^{-3}$ s$^{-1}$. For all other measurements, including those most relevant for understanding atmospheric processes on Titan, CH$_4$ gas delays the freezing to such an extent that the crystallization process cannot be observed to completion. It is, however, possible to estimate the effect of CH$_4$ incorporation on the freezing rate constant and hence freezing time of C$_2$H$_6$. Assuming that the temperature dependence of $J_{ethane}$ is equal to that of water, $J_{water}$, at $\sim -37.5$ C, the temperature at which $J_{water}$ is $\sim 10^8$ cm$^{-3}$ s$^{-1}$, a change in the ambient temperature of 1 K would lead to a change in $J_{ethane}$ of about one order of magnitude.$^{169,171}$ A freezing point depression of $\sim 5$ K as estimated for a droplet composed of 20% CH$_4$ (Table 3.1) could therefore feasibly decrease the freezing rate constant at 78 K by several orders of magnitude compared with that for a pure C$_2$H$_6$ droplet. This would mean that while a pure 1 $\mu$m radius C$_2$H$_6$ droplet would freeze within one hour, the freezing time of a mixed-composition droplet could be extended to several days. It should be noted that the freezing kinetics also depend on several substance-specific properties,$^{131}$ and that these factors have not been considered here as their quantification is beyond the scope of this study.

Table 3.1: The freezing points of pure C$_2$H$_6$ and C$_2$H$_6$/CH$_4$ mixtures

<table>
<thead>
<tr>
<th>CH$_4$ mole fraction</th>
<th>Freezing point / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>89.9</td>
</tr>
<tr>
<td>0.1</td>
<td>87.5</td>
</tr>
<tr>
<td>0.2</td>
<td>85.2</td>
</tr>
</tbody>
</table>

3.3.3 Influence of Aerosols of Trace Species on C$_2$H$_6$ Crystallization

A wide range of trace species, including C$_2$H$_2$ and CO$_2$, are present in the condensed phase as aerosols in the lower atmosphere of Titan.$^{117}$ Many of these aerosols are formed by condensation of the products of CH$_4$/N$_2$ photochemistry in Titan’s stratosphere.$^{23,38}$ Such aerosols are thought to play an important role as condensation and crystallization nuclei in the formation and evolution of CH$_4$ and C$_2$H$_6$ clouds.$^{109}$ Here we first demonstrate, that the presence of C$_2$H$_2$
Figure 3.6: The temporal evolution (top to bottom) of the ν9 fundamental during heterogeneous freezing of supercooled C2H6 droplets induced by C2H2 aerosols. The droplets were formed in (A) pure N2 gas, (B) a N2/CH4 atmosphere with yCH4 = 0.007, (C) a N2/CH4 atmosphere with yCH4 = 0.011, and (D) a N2/CH4 atmosphere with yCH4 = 0.025. The presence of CH4 gas decreases the freezing rates.

and CO2 aerosols significantly increase the freezing rate of supercooled C2H6 droplets. Then the effect of aerosols of C2H2 and CO2, in the absence and presence of CH4 gas is discussed, in order to compare the ice-nucleating effectiveness of the two species for supercooled C2H6 droplets, and to investigate the occurrence of phase I solid C2H6 during heterogeneous freezing.

Figs. 3.6-3.8 show the time evolution of the heterogeneous freezing of supercooled C2H6 in the presence of C2H2 aerosols and CH4 gas (yCH4 = 0, 0.007, 0.011 and 0.023, parts A-D). Owing to its relatively high sublimation temperature of 189 K, C2H2 immediately forms solid aerosol particles upon injection into the cell in these experiments. These solid particles act as condensation nuclei and then as freezing nuclei for C2H6. It can be seen that crystallization is significantly faster in the presence of C2H2 aerosols than for homogeneous crystallization of pure C2H6: crystallization is completed in less than two minutes in the presence of C2H2 (part A in Figs. 3.6-3.8), while in the absence of C2H2 it takes ~ 10-15 minutes to observe the first signs of freezing (part A in Figs. 3.2-3.4).
Figure 3.7: Analogous to Fig. 3.6, but for the $\nu_6$ band. Only part A shows features of $\text{C}_2\text{H}_6$ phase I at 1365 cm$^{-1}$. The sharp peaks below 1370 cm$^{-1}$ in B-D arise from rovibrational transition of cold $\text{CH}_4$ gas (see also Fig. 3.1B).

Figure 3.8: Analogous to Fig. 3.6, but for the $\nu_8$ band at 1465 cm$^{-1}$. The additional sharp peaks in B-D (not present in A) arise from rovibrational transitions of cold $\text{CH}_4$ gas.
Figure 3.9: The temporal evolution (top to bottom) of the $\nu_9$ fundamental during heterogeneous freezing of supercooled C$_2$H$_6$ droplets induced by CO$_2$ aerosols. The droplets were formed in (A) pure N$_2$ gas, (B) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.007$, (C) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.011$, and (D) a N$_2$/CH$_4$ atmosphere with $y_{CH_4} = 0.025$. The presence of CH$_4$ gas decreases the freezing rates.

Figure 3.10: Analogous to Fig. 3.9, but for the $\nu_8$ band. The additional sharp peaks in B-D (not present in A) arise from rovibrational transitions of cold CH$_4$ gas.
The heterogeneous freezing experiment was repeated in the presence of CO$_2$ aerosol particles, in order to compare the ice-nucleating effectiveness of the two types of particles. Figs. 3.9 and 3.10 part A show the crystallization of C$_2$H$_6$ in the presence of CO$_2$ aerosols in a N$_2$ atmosphere. It can be seen that, as was found for C$_2$H$_2$ aerosols, crystallization of C$_2$H$_6$ is significantly accelerated compared to homogeneous crystallization (part A in Figs. 3.2-3.4). However, it is found that the heterogeneous freezing of supercooled C$_2$H$_6$ is clearly faster in the presence of C$_2$H$_2$ nuclei than CO$_2$ nuclei for the same total amount of C$_2$H$_2$ and CO$_2$ (Figs. 3.6 and 3.8 vs. Figs. 3.9 and 3.10). This also holds even if the total amount of CO$_2$ is increased to more than twice that of C$_2$H$_2$ (not shown). This clearly demonstrates that C$_2$H$_2$ aerosols are more effective heterogeneous freezing nuclei for C$_2$H$_6$ than CO$_2$ aerosols. There are many factors that could contribute to such a substance-specific effect on the nucleation rate. It is possible that the total surface area of the ensembles of nuclei is different even if the total amount of C$_2$H$_2$ and CO$_2$ is the same. Although the total surface area cannot be measured, this explanation seems rather unlikely, firstly because of the similar condensation behavior of C$_2$H$_2$ and CO$_2$, and secondly because the same behavior is observed even if the CO$_2$ amount exceeds that of C$_2$H$_2$ by more than a factor of two. Instead the difference is attributed to the contrasting surface properties of the two types of nuclei, which is supported by the results shown in Fig. 3.11.

Fig. 3.11 shows the evolution of (A) the $\nu_5$ bending mode of C$_2$H$_2$ and (B) the $\nu_2$ bending mode of CO$_2$ during the freezing of C$_2$H$_6$ in a N$_2$ atmosphere (see also part A in Figs. 3.6-3.8 and Figs. 3.9 and 3.10). Pure C$_2$H$_2$ is known to form a polycrystalline structure with unstructured IR bands under temperature and pressure conditions similar to those used here.\textsuperscript{161} In these measurements, however, annealing of the C$_2$H$_2$ particles during C$_2$H$_6$ condensation gives rise to a change in the crystal structure of the particles, as can be seen from the band in Fig. 3.11A at $t = 1$ s, which is characteristic of crystalline orthorhombic C$_2$H$_2$.\textsuperscript{161} The orthorhombic structure, however, is not stable over time and undergoes a phase transition (Fig. 3.11A, $t > 1$ s) back to a polycrystalline structure, evident from the broad and only slightly structured bands.\textsuperscript{161} This phase transition is likely to be induced by a lattice mismatch between the crystalline orthorhombic C$_2$H$_2$ core and the crystalline C$_2$H$_6$ shell which is
Figure 3.11: Time evolution (top to bottom) of (A) the $\nu_5$-$\text{C}_2\text{H}_2$ band and (B) the $\nu_2$-$\text{CO}_2$ band during the crystallization of $\text{C}_2\text{H}_6$ in mixed $\text{C}_2\text{H}_6/\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_6/\text{CO}_2$ aerosols, respectively. The $\text{C}_2\text{H}_2$ cores have a crystalline orthorhombic structure at $t = 1\ \text{s}$. Over time, they convert into a polycrystalline form. The $\text{CO}_2$ cores have a cubic crystalline structure which does not change over time.

formed over time (see Figs. 3.6-3.8 part A at $t > 1\ \text{s}$). $\text{CO}_2$, in contrast, freezes in the stable crystalline cubic structure (Fig. 3.11B) and does not change structure over time as a result of $\text{C}_2\text{H}_6$ crystallization (Figs. 3.9 and 3.10 part A).$^{172,173}$

As outlined above, $\text{CO}_2$ nuclei are cubic crystalline and their structure is unaffected by the presence of $\text{C}_2\text{H}_6$ (Fig. 3.11B). The structure of $\text{C}_2\text{H}_2$ nuclei, by contrast, is much more flexible, not perfectly crystalline, and is influenced by the presence of $\text{C}_2\text{H}_6$ (Fig. 3.11A). The less ordered surface of $\text{C}_2\text{H}_2$ is likely to provide more nucleation sites than the ordered crystalline $\text{CO}_2$ surface,$^{174}$ explaining the higher nucleation rate and shorter crystallization time in the presence of $\text{C}_2\text{H}_2$.

The size distribution of the aerosols of the trace species is not well known for these mea-
urements because the particles are too small (< 100 nm in diameter) to produce a scattering signature suitable for precise comparison with Mie theory. The rate of heterogeneous nucleation depends strongly on the nuclei size distribution, and hence the rate constant for the heterogeneous nucleation of supercooled C$_2$H$_6$ droplets cannot be accurately determined from these measurements.\textsuperscript{168} We thus refrain from deriving freezing rate constants from these data.

In Section 3.3.2 it has been demonstrated that CH$_4$ gas, which is ubiquitous in Titan’s atmosphere, strongly decreases freezing dynamics of homogeneous freezing. The question is if the same applies for heterogeneous crystallization. In these measurements the effect of CH$_4$ gas was examined in order to compare the sensitivity of the IR bands of C$_2$H$_6$ to freezing, and to establish whether the occurrence of phase I solid C$_2$H$_6$ depends on the presence of CH$_4$ gas in the case of heterogeneous nucleation.

Figs. 3.6-3.10 show the influence of CH$_4$ gas on the rate of heterogeneous freezing. Again, any one of the $\nu_9$, $\nu_6$ or $\nu_8$ bands of C$_2$H$_6$ can in principle be used to compare the rate of freezing as the amount of CH$_4$ gas is varied, however it is important to note the differing sensitivities of the $\nu_9$, $\nu_6$ and $\nu_8$ bands to the evolving phase of the particles. For example, the narrow features of the $\nu_9$ band for solid C$_2$H$_6$, which contrast strongly with the broad, featureless shape of the $\nu_9$ band which arises from liquid C$_2$H$_6$, make this band particularly useful for monitoring liquid to solid phase changes via band shape analysis, while the difference between the band shapes for the solid and liquid phase are less pronounced for the $\nu_6$ and $\nu_8$ bands. For example, by comparing part B of Figs. 3.6, 3.7, and 3.8 at 134 s, it can be seen that the onset of crystallization can be observed more clearly by examining the $\nu_9$ than the $\nu_6$ or $\nu_8$ bands of C$_2$H$_6$.

Comparing part A with part B-D of Figs. 3.6-3.10 one can see that the crystallization rate decreases with increasing $y_{\text{CH}_4}$, and for CH$_4$ gas mole fractions relevant to Titan (part C in Figs. 3.2-3.4, and part D in Figs. 3.6-3.10) the onset of heterogeneous freezing was not observed on the timescale of the experiment, as was the case for homogeneous freezing. It is interesting to note that in the presence of CO$_2$, even a low $y_{\text{CH}_4}$ of 0.007 decreases the crystallization to such an extent that onset of freezing can only be observed towards the end of the experiment (Figs. 3.9 and 3.10 part B, $t = 2347$ s).
A quantitative analysis of the influence of gas-phase CH$_4$ on the kinetics of heterogeneous crystallization of supercooled C$_2$H$_6$ droplets in the presence of C$_2$H$_2$ or CO$_2$ is again not possible from these measurements. Only in the case of freezing in the absence of gas-phase CH$_4$ and for $y_{\text{CH}_4} = 0.007$ (Figs. 3.6-3.8, parts A and B) is the phase transition complete within the timescale of the experiment, which is required for the accurate determination of the rate constant for this process. Under the conditions relevant for Titan ($y_{\text{CH}_4} = 0.015$ and higher), for which freezing rates would be of interest, freezing is not completed on the timescale of the experiment even for heterogeneous freezing, and hence determination of the freezing rate constants is not possible.

As is the case for homogeneous freezing, in the absence of CH$_4$ heterogeneous crystallization of phase II C$_2$H$_6$ in the presence of either C$_2$H$_2$ or CO$_2$ is observed to proceed via the metastable phase I (see for example Fig. 3.6A). For heterogeneous freezing in the presence of CH$_4$ gas under otherwise identical conditions, clear evidence of phase I C$_2$H$_6$ is not observed (see for example Fig. 3.6B and C). This difference in freezing behavior could be a consequence of the addition of CH$_4$ to the particles and thus provides further evidence that CH$_4$ is incorporated into the supercooled ethane droplets.

The higher crystallization rate of heterogeneous freezing allows us to observe the freezing of C$_2$H$_6$ aerosols in the presence of gas-phase CH$_4$ almost to completion (Figs. 3.6-3.8, part B). As no significant difference is observed between the spectra of pure C$_2$H$_6$ and initially mixed-composition C$_2$H$_6$/CH$_4$ aerosols after crystallization is complete (Figs. 3.6-3.8, parts A and B), it is likely that most of the CH$_4$ is excluded from the mixed composition C$_2$H$_6$/CH$_4$ droplets as they freeze; the formation of a mixed crystalline phase would be expected to give rise to band shifts and changes in band intensities.

The IR bands of CO$_2$ are exceptionally sensitive to phase changes and to mixing with other substances (ethane) due to strong vibrational exciton coupling. Therefore, the CO$_2$ IR bands can provide information on what happens to the crystallization nuclei during the freezing process. Fig. 3.11 includes sketches of the expected structure of the mixed-composition aerosols. The CO$_2$ absorption bands for the mixed-composition particles are the same as those for pure CO$_2$ aerosols (Fig. 3.11B), revealing that CO$_2$ does not mix with C$_2$H$_6$ and consistent with a
core-shell particle structure. Fig. 3.11A shows that the C$_2$H$_2$ absorption bands for the mixed-composition particles are also the same as those for pure C$_2$H$_2$ aerosols (crystalline aerosol particles at early times, and polycrystalline particles at later times), revealing that C$_2$H$_2$ also does not mix with C$_2$H$_6$ and consistent with a core-shell particle structure. Furthermore, it was found that the presence of CH$_4$ gas has no effect on the appearance of the C$_2$H$_2$ and CO$_2$ absorption bands (not shown), again demonstrating that C$_2$H$_2$ and CO$_2$ do not co-crystallize with C$_2$H$_6$. This is significant as mixing would have an impact on the role of the nuclei and the associated freezing kinetics. The observation of the IR spectra of the trace species even allows us to draw conclusions about the particle shape. In these measurements the observed IR absorption bands are consistent with a globular shape for the C$_2$H$_2$ cores and an elongated shape for the CO$_2$ cores.

3.3.4 Influence of Freezing Mechanism on C$_2$H$_6$ Crystallization

Measurements were carried out to clarify whether the rate of heterogeneous crystallization depends on the nucleation mechanism, representing the first experimental investigation of the role of freezing mechanism under conditions relevant to Titan. The freezing of supercooled C$_2$H$_6$ droplets was investigated under conditions of immersion and contact nucleation, both of which are likely to be relevant on Titan.

Supercooled C$_2$H$_6$ and C$_2$H$_6$/CH$_4$ droplets were exposed to solid C$_2$H$_2$ particles using two distinct approaches. In the first approach the C$_2$H$_2$ gas was premixed with the C$_2$H$_6$ gas prior to injection into the cell (as for all measurements discussed in Sections 3.3.1-3.3.3). In this case C$_2$H$_2$ freezes immediately after injection and C$_2$H$_6$ gas later condenses onto the frozen nuclei, giving rise to a core-shell structure (see Fig. 3.11). This approach is therefore expected to simulate an immersion freezing mechanism, as illustrated in Fig. 3.12A. In the second approach, C$_2$H$_2$ and C$_2$H$_6$ gas are injected separately through two individual valves. Simultaneous injection of the two gases is equivalent to the first approach and also mimics immersion freezing. However, if a time delay between the injections of the two gases is introduced (sequential injection), the C$_2$H$_2$ particles will have time to diffuse away from the region of the cell where gases are injected, and pure C$_2$H$_6$ droplets will condense. It is therefore expected that as the time delay is increased a contact freezing mechanism will begin to dominate, as illustrated in
Figure 3.12: Illustration of crystallization of supercooled C$_2$H$_6$ droplets (open circles) in the presence of C$_2$H$_2$ aerosols (filled black circles) via (A) immersion and (B) contact freezing of supercooled C$_2$H$_6$ in the presence of C$_2$H$_2$ nuclei (black circles). The particle clouds spread down the cell over time.

Fig. 3.13 shows the freezing of C$_2$H$_6$ droplets in the presence of C$_2$H$_2$ nuclei for premixed gas injection (part A), simultaneous injection (injection time delay, $\Delta t = 0$ ms, part B), and sequential injection ($\Delta t = 5920$ ms, part C). That a change in the mixing state of the aerosols, and hence a change in the freezing mechanism, is indeed achieved by changing the injection approach in this way is evident from the shape of the $\nu_5$ band of C$_2$H$_2$ at $\sim 770$ cm$^{-1}$ (Fig. 3.14). In the case of premixed or simultaneous injection (spectra shown in Fig. 3.14A and B, respectively), features of crystalline orthorhombic C$_2$H$_2$ nuclei are observed, consistent with annealing by condensation of C$_2$H$_6$ onto the C$_2$H$_2$ aerosols, as discussed in Section 3.3.3. In the case of sequential injection with $\Delta t = 5920$ ms (Fig. 3.14C), C$_2$H$_2$ is not annealed and occurs in the usual polycrystalline structure, consistent with separate condensation of C$_2$H$_6$.^{161}

As expected, the freezing timescales are equivalent for the premixed and the simultaneous injection measurements, but differ when sequential injection is used (Fig. 3.13). In the latter
Figure 3.13: Temporal evolution the $\nu_9$ band of $C_2H_6$ in a $N_2/CH_4$ gas atmosphere with $y_{CH_4} = 0.011$ for (A) premixed injection of $C_2H_2/C_2H_6$, (B) separate but simultaneous injection of $C_2H_2$ and $C_2H_6$ ($\Delta t = 0$ ms), and (C) sequential injection of $C_2H_2$ followed by $C_2H_6$ ($\Delta t = 5920$ ms). Different freezing rates indicate a different nucleation mechanism.

case the onset of freezing is delayed by $\sim 20$ minutes, indicating that contact freezing is less efficient than immersion freezing under the measurement conditions. The time required for the separate $C_2H_2$ and $C_2H_6$ particle clouds to mix has not been considered for the times indicated in Fig. 3.13, since this cannot be accurately quantified. This will lead to a trivial delay to contact freezing compared to immersion freezing in these experiments. Nevertheless, an estimate of the cloud mixing time reveals that this alone cannot explain the observed delay to the onset of crystallization of almost 20 minutes for contact freezing compared with immersion freezing (Fig. 3.13), and that there is indeed a difference between the two mechanisms. It should be noted that contact freezing and immersion freezing are sensitive to factors such as temperature and particle size,\textsuperscript{131,177} and as in most other experimental studies a quantitative evaluation of the influence of these factors is not possible for these measurements.
Figure 3.14: The $\nu_5$-bending mode of C$_2$H$_2$ recorded immediately after C$_2$H$_6$ injection for (A) premixed injection of C$_2$H$_2$/C$_2$H$_6$, (B) separate but simultaneous injection of C$_2$H$_2$ and C$_2$H$_6$, and (C) sequential injection of C$_2$H$_2$ followed by C$_2$H$_6$ ($\Delta t = 5920$ ms). The spectra in parts A and B exhibit features of orthorhombic C$_2$H$_2$, which is caused by annealing due to condensation of C$_2$H$_6$ onto the C$_2$H$_2$ nuclei. The spectrum in part (C) shows the broad features of polycrystalline C$_2$H$_2$. Annealing is not possible in this case because C$_2$H$_2$ and C$_2$H$_6$ do not form core-shell structures.

3.3.5 Role of N$_2$ in the Freezing Dynamics of C$_2$H$_6$ Droplets

N$_2$ is the major gas-phase component in Titan’s atmosphere. To describe the possible influence of N$_2$ on the freezing we have repeated all experiments for the above-described binary, ternary and quaternary systems replacing N$_2$ with He. Fig. 3.15 shows that for supercooled pure C$_2$H$_6$ droplets, freezing in He is only slightly faster than in N$_2$. It was also determined that the equivalent effect is found for freezing in the presence of CH$_4$ gas and for heterogeneous freezing (not shown). Compared to the influence of CH$_4$ gas reported in Sections 3.3.2 and 3.3.3, it can be seen that the influence on the freezing kinetics of changing the bath gas from N$_2$ to He (mole fraction $> 0.924$) is much less significant compared to the influence if CH$_4$ (mole fraction $< 0.026$).

Slightly lower freezing rates may be observed in N$_2$ as a result of incorporation of minor amounts of this gas into the droplets (not expected for He at 78 K). As in the case of CH$_4$, incorporation of N$_2$ would lead to a depression of the freezing point of the droplets, and hence
Figure 3.15: Temporal evolution the $\nu_9$ band of C$_2$H$_6$ for pure supercooled C$_2$H$_6$ droplets in (A) He and (B) N$_2$. Crystallization is slightly faster in He than in N$_2$.

to a reduction in the freezing rate (see discussion of freezing point depression in Section 3.3.2). The relatively minor influence of N$_2$ on the freezing kinetics compared with CH$_4$ would be consistent with a smaller amount of N$_2$ being incorporated into the droplets; from additional experiments$^{113}$ an upper limit of 7% on the amount of N$_2$ incorporated into pure C$_2$H$_6$ droplets is estimated (experimental uncertainty; see also the work by Guedes et al.$^{178}$, albeit for a higher temperature). Our measurements do not yield any spectroscopic evidence for the incorporation of N$_2$ into the C$_2$H$_6$ droplets; although N$_2$ is very weakly IR active in the liquid phase, the absorption features are not sufficiently intense to be observable in the spectra.

It should be noted that some dependence of the freezing rate on the chosen bath gas will also arise from the differences in the physical properties of N$_2$ and He, for example the thermal conductivity of N$_2$ is lower than that of He at 78 K$^{179,180}$ and diffusion of hydrocarbons is faster in He than in N$_2$$^{181}$ and therefore cooling during particle formation and crystallization might be more efficient in He than in N$_2$. Further, it was found that larger particles form at early times in He than in N$_2$. We hope that we will be able to consider such factors in detail in future studies using an alternative experimental approach.

53
3.4 Conclusions

Spectroscopic studies of the homogeneous and heterogeneous freezing of supercooled C$_2$H$_6$ droplets have been carried out under conditions chosen to mimic those in Titan’s lower atmosphere, where C$_2$H$_6$ aerosols and C$_2$H$_6$ clouds are thought to play an important role. The IR spectra of pure C$_2$H$_6$ and mixed C$_2$H$_6$/CO$_2$ and C$_2$H$_6$/C$_2$H$_2$ aerosols are reported for the extended frequency range of 3300 to 650 cm$^{-1}$. The phase-dependent behavior of the C$_2$H$_6$ $\nu_8$, $\nu_6$, and $\nu_9$ fundamental modes for C$_2$H$_6$ aerosols, which appear at 1465 cm$^{-1}$, 1370 cm$^{-1}$, and 820 cm$^{-1}$, respectively, has been reported, providing essential data for planetary remote sensing studies, as does the observation that the CH-stretching bands above 2700 cm$^{-1}$ are insensitive to phase.

The spectral signature and occurrence of solid phase I C$_2$H$_6$ have been studied. The spectrum of phase I in the region of the $\nu_6$ and $\nu_8$ bands is reported for the first time, and it has been observed that under these conditions the presence of CH$_4$ seems to influence whether the freezing of supercooled C$_2$H$_6$ droplets proceeds directly or via the metastable phase I C$_2$H$_6$.

The ice-nucleating effectiveness of two types of particles likely to be important in Titan’s atmosphere, C$_2$H$_2$ and CO$_2$ aerosols, has been compared for supercooled C$_2$H$_6$ droplets, and the observed difference rationalized in terms of the crystal structure of the particles. C$_2$H$_2$ aerosols are the more effective ice nuclei for C$_2$H$_6$, attributed to the fact that they have a less ordered surface structure than CO$_2$ particles. The influence of nuclei composition on the efficiency of heterogeneous nucleation is a key question in understanding cloud processes.$^{182}$ The first experimental investigation of the influence of freezing mechanism on the rate of crystallization of supercooled C$_2$H$_6$ droplets under conditions relevant to Titan has been performed. Immersion freezing was found to be more efficient than contact freezing under these conditions. Together with the major results reported in previous contributions by Sigurbjörnsson and Signorelli,$^{111}$ the present study shows that CH$_4$ gas significantly delays the freezing of C$_2$H$_6$ droplets,$^{183}$ and provides a detailed picture of the microphysical behavior of C$_2$H$_6$ cloud droplets on Titan.

It was not possible to quantify two important parameters in the present study. Firstly, the achievable observation times were too short to determine accurate freezing rate constants for
the long-lived supercooled C$_2$H$_6$ droplets. Secondly, it was not possible to precisely measure the composition of the C$_2$H$_6$/CH$_4$/(N$_2$) droplets. In order to address these points an alternative experimental approach capable of studying droplet freezing over an extended period of time is currently being developed and efforts were made to calculate the vapor-liquid-equilibrium (VLE) composition of binary and ternary mixtures relevant to Titan.\textsuperscript{5,184} The results of these calculations are briefly summarized here.

Monte-Carlo (MC) simulations of the binary system CH$_4$-N$_2$ confirm that liquid CH$_4$-N$_2$ droplets consist of up to $\sim$ 70\% CH$_4$ and 30\% N$_2$ (for $y_{\text{CH}_4} = 0.025$) under conditions similar those used in the experiments here ($p \sim 550$ mbar, $T = 78$ K, $y_{\text{CH}_4} = 0, 0.007, 0.011, 0.025$).\textsuperscript{184} The same composition was earlier experimentally estimated by Wang et al.\textsuperscript{113}

To better understand the observations made and described in this chapter regarding supercooling and stabilization of C$_2$H$_6$ droplets, as well as to determine particle compositions, MC simulations were performed to simulate the binary systems N$_2$-C$_2$H$_6$ and CH$_4$-C$_2$H$_6$, and the ternary systems He-CH$_4$-C$_2$H$_6$ and N$_2$-CH$_4$-C$_2$H$_6$.

Earlier in this chapter, an upper limit of 7\% was set on the incorporation of N$_2$ into C$_2$H$_6$ aerosol particles ($T = 78^\circ$K, $p = 550$ mbar).\textsuperscript{118} The result for the MC calculations of the binary system N$_2$-C$_2$H$_6$ show that $\sim$ 4.3\% N$_2$ is incorporated into supercooled liquid C$_2$H$_6$ droplets at 78 K. Therefore MC calculations and experimental findings are in good agreement. The calculations also show that this value does not vary much with increasing temperature and pressure ($78$ K $\leq T \leq 93.1$ K, $550$ mbar $\leq p \leq 1447$ mbar).

Calculations for the ternary system He-CH$_4$-C$_2$H$_6$ and binary system CH$_4$-C$_2$H$_6$ were based on the experiments described in this chapter ($T = 78$ K, $p = 550$ mbar, $y_{\text{CH}_4} = 0.007, 0.011, 0.015, 0.025$, with $p = p_{\text{CH}_4} = 3.85, 6.05, 8.25, 13.75$ mbar for the binary system). The results show that the droplet composition in the binary and ternary system is essentially the same and that He is not incorporated into C$_2$H$_6$ droplets as was assumed earlier. A mole fraction of $y_{\text{CH}_4} = 0.007$ in the gas phase results in a composition of $\sim$ 82.8\% C$_2$H$_6$ and $\sim$ 17.2\% CH$_4$ of the mixed CH$_4$-C$_2$H$_6$ droplets, matching the initial experimental estimate of 20\%.\textsuperscript{183} The CH$_4$ mole fraction in the liquid ($x_{\text{CH}_4}$) increases with increasing $y_{\text{CH}_4}$. A mole fraction of $y_{\text{CH}_4} = 0.015$ in the gas phase results in a composition of $\sim$ 58.2\% C$_2$H$_6$ and $\sim$ 41.8\% CH$_4$.\textsuperscript{55}
According to Eq. 3.1 this results in a freezing point $T_{fus} = 80.1$ K for these droplets, 10.25 K below the freezing point of pure C$_2$H$_6$.

For the same conditions ($T = 78$ K, $p = 550$ mbar, $y_{\text{CH}_4} = 0.007, 0.011, 0.015, 0.025$) the composition of droplets of the ternary system N$_2$-CH$_4$-C$_2$H$_6$, the system most relevant to Titan, was calculated. From our experimental measurements we expected a minor incorporation of N$_2$ and a major incorporation of CH$_4$. However, the MC calculations showed otherwise: C$_2$H$_6$ droplets incorporate a mixture of N$_2$ and CH$_4$. This mixture has a rough ratio of CH$_4$:N$_2 \approx 3:1$, and the amount of this mixture incorporated into the ethane droplets is proportional to $y_{\text{CH}_4}$ in the gas phase. This can lead to a substantial incorporation of N$_2$, much higher than the 4.3% for the binary system N$_2$-C$_2$H$_6$. Even though we cannot confirm these theoretical results experimentally, the ternary system N$_2$-CH$_4$-C$_2$H$_6$ is a rather simple system, and we believe that our MC calculations are correct and our results trustworthy. Further and detailed results of the MC studies can be found in Luckhaus et al.\textsuperscript{5}
Chapter 4

Phase Behavior of Propane and n-Pentane Aerosol Particles Under Conditions Relevant to Titan

4.1 Introduction

In the previous Chapter the focus was set on ethane (C$_2$H$_6$) aerosol particles and the influence of methane (CH$_4$) gas and trace aerosols on the phase behavior. This was of great interest since CH$_4$ and C$_2$H$_6$ are two of the most important cloud forming species on Titan. However, Titan’s photochemistry is rich and C$_2$H$_6$, though being the second most abundant species in Titan’s atmosphere, is not the only photochemical product. Other hydrocarbons, such as propane (C$_3$H$_8$), butane (C$_4$H$_{10}$), and pentane (C$_5$H$_{12}$) can possibly form and condense to aerosols in Titan’s lower atmosphere (note that so far only the formation of C$_3$H$_8$ on Titan could be confirmed$^{[186,187]}$).

The present chapter is devoted to the study of the phase behavior of C$_3$H$_8$ and normal-pentane (n-C$_5$H$_{12}$) aerosol condensates under conditions that are representative of Titan’s troposphere and lower stratosphere. So far, C$_5$H$_{12}$ has not been detected on Titan, neither as a gas nor in condensed form, although it is a likely product of Titan’s CH$_4$ photochemistry. Navarro-Gonzalez et al. simulated corona discharges in laboratory experiments and identified n-C$_5$H$_{12}$ and its isomers amongst other hydrocarbons, including C$_2$H$_6$ and C$_3$H$_8$, as prod-
This demonstrates that \( C_5H_{12}\) could exist in Titan’s atmosphere and hence, at high enough concentrations, could condense to form aerosol particles. In contrast to \( C_5H_{12}\), \( C_3H_8\) gas has already been identified as a product of Titan’s \( CH_4\) photochemistry\(^{117,186-188}\) with a stratospheric volume mixing ratio of \( 4.2 \pm 0.5 \times 10^{-7}\).\(^{187}\) So far the existence of condensed \( C_3H_8\) has not been confirmed,\(^{33}\) but it is believed to be one of the main constituents of Titan’s lakes, with an estimated mole fraction of 7-8\%\(^{138}\). \( C_3H_8\) condensation to aerosols has not been observed directly, but it is clearly expected to occur around or below an altitude of 60 km at a relatively high rate (total atmospheric pressure = 40 mbar, \( T = 81\) K).\(^{33}\) Since acetylene (\( C_2H_2\)) is expected to form aerosol particles in the same region mixed \( C_3H_8\)-\( C_2H_2\) systems have to be taken into account, in particular with regard to the crystallization behavior of \( C_3H_8\) aerosol condensates.\(^{33}\) Titan’s temperature profile allows for the existence of \( C_3H_8\) in the liquid as well as the solid phase. Although not part of the present study, we note that the chemistry of solid \( C_3H_8\) on Titan has been the subject of several laboratory studies. This includes the irradiation of \( C_3H_8\) ice as well as chemical reaction of \( C_3H_8\) with radicals such as the ethynyl radical, \( C_2H\), or the butadiynyl radical, \( C_4H\), which are abundant in many astrophysical environments.\(^{97,189,190}\)

The crystallization behavior of \( C_3H_8\) and \( n-C_5H_{12}\) aerosol condensates under conditions relevant to Titan’s atmosphere is the focus of this chapter. Owing to their very different melting points, \( C_3H_8\) (\( T_{fus} = 85.5\) K; \( T_{trip} = 85.52\) K)\(^{145,191}\) and \( n-C_5H_{12}\) (\( T_{fus} = 143.4\) K; \( T_{trip} = 143.48\) K)\(^{147,148}\) are interesting to compare. Crystallization seems to be fast for \( n-C_5H_{12}\) but exceptionally slow in the case of \( C_3H_8\).\(^{192,193}\) Bulk \( C_3H_8\) was found to crystallize in the space group \( P2_1/n\) and bulk \( n-C_5H_{12}\) in the space group \( Pbcn\).\(^{192,194}\) In the present work, rapid-scan mid-infrared (mid-IR) spectroscopy is used to monitor phase transitions in \( C_3H_8\) and \( n-C_5H_{12}\) aerosol condensates and to determine crystallization rate constants. The influence of nitrogen (\( N_2\)) – the major gaseous constituent of Titan’s atmosphere – and of other species, such as \( C_2H_2\), carbon dioxide (\( CO_2\)), and water (\( H_2O\)), is reported and discussed. Section 4.2 briefly describes the experimental set-up and conditions followed by the results for \( C_3H_8\) and \( n-C_5H_{12}\) aerosols in Sections 4.3.1 and 4.3.2 respectively.
4.2 Experimental

The experimental set-up, sample preparation and the general experimental conditions are described in Chapter 2.1. Here the more specific details on the experimental conditions to study the phase behavior of C\textsubscript{3}H\textsubscript{8} and \textit{n}-C\textsubscript{5}H\textsubscript{12} aerosol particles in presence and absence of the trace species C\textsubscript{2}H\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}O are given.

Prior to sample injection the cooling cell was filled at pressures of 550 or 800 mbar with either He or N\textsubscript{2} as bath gas and pre-cooled to 78 K. At 78 K a pressure of 550 mbar matches the atmospheric conditions at an altitude of \textasciitilde 18 km on Titan. Pure or multicomponent aerosol particle ensembles were generated by injecting warm (\textit{T} = 293 K) sample gases (\textasciitilde 0.025-0.75\% diluted in He or N\textsubscript{2}) into the cell.

For the mixed aerosols, the ratios of C\textsubscript{3}H\textsubscript{8} or \textit{n}-C\textsubscript{5}H\textsubscript{12} to CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{2}, or H\textsubscript{2}O were typically 4:1, 3:1, 2:1 or 1:1. Pre-mixed as well as sequential injection experiments were performed. The time delay for sequential measurements was \( \Delta t = 0.75-1.0 \) s (valve opening time = 0.5 s).

In an attempt to obtain the IR spectra of liquid C\textsubscript{3}H\textsubscript{8} and \textit{n}-C\textsubscript{5}H\textsubscript{12} droplets, their spectra were also recorded above the respective melting points of the bulk by adjusting the cell temperature with a heating unit.

Mid-IR absorption spectra of the aerosols were recorded in the region from 8000 to 500 cm\textsuperscript{-1}. The spectra were recorded with a spectral resolution of 0.5 cm\textsuperscript{-1} at time intervals between 2 and 300 seconds, starting immediately after particle formation. Total measurement times were ranging from 20 minutes to 2 hours.

In addition to \textit{n}-C\textsubscript{5}H\textsubscript{12} aerosol spectra, the IR spectrum of liquid bulk \textit{n}-C\textsubscript{5}H\textsubscript{12} was also recorded at room temperature with an attenuated total reflectance (ATR) FTIR spectrometer (Spectrum\textsuperscript{TM} 400, PerkinElmer) with a spectral resolution of 1 cm\textsuperscript{-1}. 
4.3 Results and Discussion

4.3.1 Propane Aerosols

4.3.1.1 Propane Aerosols in He and N\textsubscript{2} Bath Gas

Figs. 4.1 to 4.3 provide a summary of the spectral features of pure and multicomponent C\textsubscript{3}H\textsubscript{8} aerosols, which were formed at 78 K by rapid injection of room temperature gas mixtures into the cold bath gases. A typical IR spectrum of pure C\textsubscript{3}H\textsubscript{8} aerosols between 3500 and 700 cm\textsuperscript{-1} is depicted in Fig. 4.1A. The corresponding band positions in the fingerprint region (see inset in Fig. 4.1A) are listed in the last column of Table 4.1 (see Coustenis et al.\textsuperscript{33} and Snyder and Schachtschneider\textsuperscript{193} for band assignments).

In order to study potential phase changes, we have recorded aerosol IR spectra as a function of time after completion of droplet/particle formation (less than 1 second after injection of
Figure 4.2: Time evolution of the IR spectra of C$_3$H$_8$ aerosols in (A) He (800 mbar) and (B) N$_2$ (800 mbar) (C$_3$H$_8$:bath gas = $\sim 10^{-5}$:1) at 78 K in the region of the $\nu_5$ and $\nu_4$ bands. The time after droplet/particle formation is indicated for each spectrum in part A and is the same for the adjacent spectrum in part B.

Sample gases) over a total observation time of about 76 minutes. Surprisingly, we did not detect any spectral changes as a function of time. This is illustrated in Fig. 4.2 for the region of the $\nu_5$ and $\nu_4$ bands around 1465 cm$^{-1}$, which is the most sensitive spectral range for discriminating between phases of condensed C$_3$H$_8$.$^{33,193,195,196}$ These measurements were performed in He bath gas (part A) and in N$_2$ bath gas (part B) because we earlier observed a strong influence of the type of bath gas on the composition and on the kinetics of phase transitions for CH$_4$ and C$_2$H$_6$ aerosols (see Chapter 3.3.5).$^{113,183,184,197}$ In the case of C$_3$H$_8$, however, the type of bath gas has no observable effect on the band shapes or band positions. Either the C$_3$H$_8$ condensates (droplets/particles) initially formed do not undergo a phase transition within the observation time, or such phase transitions cannot be detected because of a lack of characteristic infrared features to distinguish between different phases.

IR spectra of crystalline and liquid C$_3$H$_8$ films$^{33,193,195,196}$ together with other C$_3$H$_8$ bulk
phase studies\textsuperscript{145,191,192,198,199} provide several hints which may be used to narrow down the possible phases of the C\textsubscript{3}H\textsubscript{8} aerosol condensates giving rise to the spectra shown in Fig. 4.2. The broad, only slightly structured, band around 1465 cm\textsuperscript{-1} is inconsistent with crystalline aerosol particles. As shown by Coustenis et al.,\textsuperscript{33} crystalline C\textsubscript{3}H\textsubscript{8} films at 80 K exhibit a distinct double band with band maxima at 1461 cm\textsuperscript{-1} and 1465 cm\textsuperscript{-1}, and not the single broad band which can be seen in Fig. 4.2. Obviously, C\textsubscript{3}H\textsubscript{8} aerosols are not formed as crystalline particles, nor do they crystallize on the timescale of our observation (Fig. 4.2). This behavior is in stark contrast with that of other hydrocarbon aerosols recently studied with our bath gas cooling cell. Pure C\textsubscript{2}H\textsubscript{6},\textsuperscript{111} n-butane (n-C\textsubscript{4}H\textsubscript{10}),\textsuperscript{200} and n-C\textsubscript{5}H\textsubscript{12} (see Section 4.3.2) aerosol condensates crystallize within only a few minutes following formation\textsuperscript{145,191,198,199} The peculiar behavior of C\textsubscript{3}H\textsubscript{8} aerosols seems to be consistent with previous findings for bulk C\textsubscript{3}H\textsubscript{8} compared with other simple hydrocarbons in terms of their melting point, glass transition, and freezing/crystallization behavior.\textsuperscript{145,191,198,199}

If it is not crystalline, the aerosol particle phase must be disordered or partially disordered, existing for example in a liquid or amorphous solid state, including glassy states. From the few IR spectra available in the literature, the appearance of the aerosol spectrum fits best with the film spectrum recorded at 77.5 K by Snyder and Schachtschneider.\textsuperscript{193} Both spectra show a broad band around 1465 cm\textsuperscript{-1} instead of the doublet characteristic of the crystalline phase, indicating that the aerosols are not composed of crystalline propane in the present measurements. Although the band observed by Snyder and Schachtschneider is slightly more structured with several additional peaks (Table 4.1), its general appearance is similar (Fig. 4.2).\textsuperscript{193} Furthermore, Snyder and Schachtschneider mentioned that “At this temperature ... C\textsubscript{3}H\textsubscript{8} was not a solid but appeared to be a very viscous liquid.” The formation of viscous liquid aerosol droplets seems very likely in the light of these observations and in particular because particle formation and cooling are fast (within less than 1 s) in our cooling cell and because the cell temperature of 78 K lies close to the melting point of C\textsubscript{3}H\textsubscript{8} \((T_{fus} = 85.5 \text{ K}; T_{trip} = 85.52 \text{ K})\textsuperscript{145,191}\) Additional measurements between 85 and 110 K, above the melting point of C\textsubscript{3}H\textsubscript{8}, produced the same spectra as at 78 K, which is again consistent with the formation of liquid droplets at 78 K.\textsuperscript{1}

\textsuperscript{1}See Chapter 3 and 5 for C\textsubscript{2}H\textsubscript{6} and n-C\textsubscript{4}H\textsubscript{10} aerosol particles, respectively.
Table 4.1: Vibrational band positions for C\textsubscript{3}H\textsubscript{8} films and aerosol in cm\textsuperscript{-1}

<table>
<thead>
<tr>
<th>Assignment\textsuperscript{[a]}</th>
<th>Thin Film, 80 K\textsuperscript{[a]}</th>
<th>Thin Film, 77 K\textsuperscript{[b]}</th>
<th>Thin Film, 77.5 K\textsuperscript{[c]}</th>
<th>Aerosol, 78 K\textsuperscript{[d]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_5)</td>
<td>1472</td>
<td>1473</td>
<td>1469</td>
<td></td>
</tr>
<tr>
<td>(\nu_4)</td>
<td>1461</td>
<td>1464</td>
<td>1465</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1459</td>
<td>1455(sh)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1449</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1441</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1429</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\nu_{18})</td>
<td>1388</td>
<td>1382</td>
<td>1389</td>
<td>1384</td>
</tr>
<tr>
<td>(\nu_6)</td>
<td>1367.5</td>
<td>1368</td>
<td>1363,1370</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1333</td>
<td>(1362(sh)), 1369</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1288(vw)</td>
<td>1290</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1262(w)</td>
<td>(1288)</td>
<td></td>
</tr>
<tr>
<td>(\nu_7, \nu_{25})</td>
<td>1155,1185</td>
<td>1155, 1185</td>
<td>1157, 1187</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1157, 1186</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1137 (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\nu_{20})</td>
<td>1050</td>
<td>1050</td>
<td>1049,1052</td>
<td></td>
</tr>
<tr>
<td>(\nu_{21})</td>
<td>918</td>
<td>918</td>
<td>917,921</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>899</td>
<td>(900)</td>
<td></td>
</tr>
<tr>
<td>(\nu_8)\textsuperscript{[c]}</td>
<td>869</td>
<td>868</td>
<td>870</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>861</td>
<td>(862(sh))</td>
<td></td>
</tr>
<tr>
<td>(\nu_{26})</td>
<td>746.5</td>
<td>745</td>
<td>747</td>
<td>747</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Coustenis et al.\textsuperscript{[33]} \textsuperscript{[b]} Goodman et al.\textsuperscript{[196]} \textsuperscript{[c]} Snyder and Schachtschneider\textsuperscript{[193]} \textsuperscript{[d]} this work, \textsuperscript{[e]} Kaiser et al.\textsuperscript{[189]} () visible only at high concentrations, sh-shoulder, w-weak, vw-very weak

Viscous liquid aerosol droplets could also explain the exceedingly slow crystallization of C\textsubscript{3}H\textsubscript{8} aerosols compared with C\textsubscript{2}H\textsubscript{6}, n-C\textsubscript{4}H\textsubscript{10}, and n-C\textsubscript{5}H\textsubscript{12} aerosols. Because the cell temperature was below the melting point of C\textsubscript{3}H\textsubscript{8}, droplets formed in a He bath gas (Fig. 4.2A) would be in a metastable supercooled liquid state. Droplets formed in N\textsubscript{2} bath gas (Fig. 4.2B) could either be in a metastable supercooled or in a stable liquid state depending on the miscibility of C\textsubscript{3}H\textsubscript{8} with N\textsubscript{2}, since binary mixtures could have a freezing point < 78 K. As corresponding miscibility data are not available at these temperatures we estimate the freezing point depression of N\textsubscript{2}-C\textsubscript{3}H\textsubscript{8} mixtures assuming ideal behavior and an enthalpy of fusion of C\textsubscript{3}H\textsubscript{8} of \(\Delta H_{fus} = 3.52 \text{ kJ mol}^{-1}\textsuperscript{[201]}\textsuperscript{[ii]}\textsuperscript{[ii]} A N\textsubscript{2} mole fraction of roughly 40% would be required to lower the freezing point of the particles to 78 K.

Solid amorphous aerosol particles are conceivable as an alternative to the liquid droplets since IR spectra of liquids and amorphous solids often resemble each other. Unfortunately,

\textsuperscript{[ii]} Estimation according to Eq. 3.1
the only IR spectrum of amorphous C$_3$H$_8$ reported in literature at $T = 4.2$ K$^{195}$ has a too low resolution and is not suitable for comparison with the aerosol spectrum. Other C$_3$H$_8$ bulk phase studies can provide some hints.$^{145,191,192,198,199}$ A glassy amorphous state is very unlikely since the only known glass transition temperature $T_g = 45.4$ K of C$_3$H$_8$ lies far below the temperature in our cooling cell.$^{199}$ Other amorphous phases cannot be completely ruled out, but no study has ever reported the formation of amorphous solid C$_3$H$_8$ under similar experimental conditions to ours. As various studies for bulk C$_3$H$_8$ clearly mention difficulties in freezing (and crystallizing) C$_3$H$_8$,$^{145,192,193,198}$ we believe that the formation of amorphous solid particles is unlikely in our experiment. In the light of what is known about bulk C$_3$H$_8$ the initial formation of supercooled viscous liquid aerosol droplets, which stay liquid over the time of the experiment, provides the most consistent explanation for our observations.

4.3.1.2 Propane Aerosols in the Presence of C$_2$H$_2$, CO$_2$, and H$_2$O

In heterogeneous freezing experiments of C$_2$H$_6$ aerosols with solid C$_2$H$_2$, CO$_2$, and H$_2$O aerosol particles acting as crystallization nuclei, we recently observed significant acceleration of the crystallization kinetics compared with pure C$_2$H$_6$ aerosols.$^{134,183,197}$ n-C$_5$H$_{12}$ aerosols show a very similar behavior (see Section 4.3.2.3), as do n-C$_4$H$_{10}$ aerosols (see Chapter 5.3.4). In an attempt to induce crystallization or other phase transitions we have carried out equivalent experiments for C$_3$H$_8$ aerosols. We performed premixed and sequential injection experiments as described in Chapter 2.1.3 (Fig. 2.2) and in Section 4.2 with either C$_2$H$_2$, CO$_2$, or H$_2$O as a second component in varying concentrations. For the sequential injection, the order of C$_3$H$_8$ and the second gas was also interchanged. All experiments were performed in both He and N$_2$ bath gases, with IR spectra recorded over total measurement times ranging from 40 minutes to 2 hours.

Figs. 4.1B and 4.3 are typical examples of IR spectra of aerosols formed at 78 K in N$_2$ from a premixed C$_3$H$_8$/C$_2$H$_2$ gas mixture. The absorption bands at 3230 cm$^{-1}$ and 773 cm$^{-1}$ correspond to the antisymmetric stretching ($\nu_3$) and the bending ($\nu_5$) mode of C$_2$H$_2$, respectively.$^{160}$ Most notably, all of the binary experiments show C$_3$H$_8$ bands that remain unchanged over time (Fig. 4.3A) and which are identical to those of pure C$_3$H$_8$ (Figs. 4.1A and 4.2); it was obviously impossible to crystallize C$_3$H$_8$ aerosol condensates or induce any other phase
Figure 4.3: Time evolution of the IR spectra of mixed C\textsubscript{3}H\textsubscript{8}/C\textsubscript{2}H\textsubscript{2} aerosols (C\textsubscript{3}H\textsubscript{8}:C\textsubscript{2}H\textsubscript{2} = 2:1) in N\textsubscript{2} (800 mbar) at 78 K. A: Region of the \nu\textsubscript{5} and \nu\textsubscript{4} bands of C\textsubscript{3}H\textsubscript{8}. B: Region of the \nu\textsubscript{5} bands of C\textsubscript{2}H\textsubscript{2} with the \nu\textsubscript{26} band of C\textsubscript{3}H\textsubscript{8} at 747 cm\textsuperscript{-1}. The time after droplet/particle formation is indicated for each spectrum in part A and is the same for the adjacent spectrum in part B.

One might argue that C\textsubscript{3}H\textsubscript{8} does not interact strongly enough with any of the other substances to produce a significant difference from experiments with pure C\textsubscript{3}H\textsubscript{8}. However, this would be at odds with the pronounced observed effects of C\textsubscript{2}H\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}O on the crystallization kinetics of C\textsubscript{2}H\textsubscript{6}, \textit{n}-C\textsubscript{4}H\textsubscript{10}, and \textit{n}-C\textsubscript{5}H\textsubscript{12} aerosols, where intermolecular interactions are similar to those in the case of C\textsubscript{3}H\textsubscript{8}. Furthermore, the profile of the C\textsubscript{2}H\textsubscript{2} bands depicted in Fig. 4.3B provides clear evidence for significant interaction with C\textsubscript{3}H\textsubscript{8}. Pure C\textsubscript{2}H\textsubscript{2} aerosols formed under the same experimental conditions are known to crystallize in a partially disordered (possibly polycrystalline) structure, with a broad unstructured band profile for the \nu\textsubscript{5} transition.
band instead of the triplet structure visible in Fig. 4.3B at \( t = 1 \) s.\textsuperscript{161} The triplet structure with maxima at 787, 772, and 736 cm\(^{-1}\) is characteristic of crystalline orthorhombic aerosol particles.\textsuperscript{161} As shown in Lang et al.\textsuperscript{197} crystalline \( \text{C}_2\text{H}_2 \) particles only form in the presence of a second condensing gas; here \( \text{C}_3\text{H}_8 \). There exist several possible microphysical structures for a particle consisting of two or more substances. The substances may exist as segregated pure components, in which case the particle architecture may be best described by either a core-shell structure or as consisting of partially-engulfed “zones” or “islands”, for example. Alternatively the two substances may mix on the molecular level. The thermodynamically-favored particle microphysical structure is determined by the subtle interplay of the relative energies of the pure and mixed substances (for example the lattice energies in the case of crystalline substances), and by the interfacial energies between the various substances and between the substances and the surrounding gas phase.\textsuperscript{202} It is also possible for the particles to be observed in metastable states in cases where formation of the most stable structure is kinetically limited on the timescale of the measurements. In such cases events such as the condensation of a second substance may provide the additional energy required for necessary structural rearrangements to occur so that the minimum energy structure may be achieved, as we believe is the case when \( \text{C}_3\text{H}_8 \) condenses onto \( \text{C}_2\text{H}_2 \) aerosols (initially resulting in the conversion of partially-disordered \( \text{C}_2\text{H}_2 \) to crystalline \( \text{C}_2\text{H}_2 \)).

We believe that the heat of condensation of the second gas provides the additional energy required to form crystalline \( \text{C}_2\text{H}_2 \) aerosols as described earlier for mixed \( \text{C}_2\text{H}_2/\text{C}_2\text{H}_6 \) aerosols. In the study with \( \text{C}_2\text{H}_6 \) it was more likely that liquid \( \text{C}_2\text{H}_6 \) condensed onto solid \( \text{C}_2\text{H}_2 \) particles, while in the present case \( \text{C}_3\text{H}_8 \) probably forms liquid droplets before \( \text{C}_2\text{H}_2 \) condenses onto them. Otherwise similar behavior is expected. As before we observe that the IR features of crystalline \( \text{C}_2\text{H}_2 \) gradually disappear, as can be seen in Fig. 4.3B. Over time the triplet structure of the crystal becomes less and less distinct, leaving behind a rather unstructured band. The latter could be the result of molecular mixing of \( \text{C}_3\text{H}_8 \) and \( \text{C}_2\text{H}_2 \) starting at their interface. In the absence of further mixing data, however, this remains a hypothesis. An alternative explanation would involve \( \text{C}_2\text{H}_2 \) transitioning into a less structured state (for example polycrystalline) to

\textsuperscript{iii}See also heterogeneous crystallization of \( \text{C}_2\text{H}_6 \) aerosol particles in Chapter 3.3.3.
minimize the interfacial energy, in a similar manner to the case discussed in Lang et al.\textsuperscript{197} This is not implausible for C\textsubscript{2}H\textsubscript{2}, for which different solid structures lie energetically close.

In summary, we find C\textsubscript{3}H\textsubscript{8} aerosols to be impossible to crystallize on the timescale of these measurements, in contrast with C\textsubscript{2}H\textsubscript{6} (Chapter 3),\textsuperscript{111,183,197} n-C\textsubscript{4}H\textsubscript{10} (Chapter 5),\textsuperscript{200} and n-C\textsubscript{5}H\textsubscript{12} aerosols (Section 4.3.2), for which crystallization happens quickly. A likely explanation for this behavior is the formation of viscous liquid C\textsubscript{3}H\textsubscript{8} droplets with possible implications for aerosols on Titan as briefly discussed in Section 4.4.

4.3.2 n-Pentane Aerosols

4.3.2.1 n-Pentane Aerosols in He and N\textsubscript{2} Bath Gas

While C\textsubscript{3}H\textsubscript{8} aerosol condensates are only slightly supercooled at 78 K (7.5 K with respect to the bulk melting point), the degree of supercooling is substantial for n-C\textsubscript{5}H\textsubscript{12} aerosol condensates under the same conditions (65.4 K below $T_{fus} = 143.4$ K).\textsuperscript{147} For other systems, such as H\textsubscript{2}O aerosols, high supercooling results in fast crystallization of the supercooled liquid droplets initially formed upon condensation.\textsuperscript{169,170} As expected the behavior of n-C\textsubscript{5}H\textsubscript{12} aerosols is similar, as demonstrated by the observed IR spectra shown in Figs. 4.4 and 4.5. In a He bath gas (Figs. 4.4B and 4.5A.1 and B.1), the crystallization occurred immediately after particle formation, and hence the spectrum of crystalline aerosol particles was observed from the beginning (Fig. 4.5A.1 and B.1). In the region between 1500 and 1350 cm\textsuperscript{-1} we see the same sharp bands and the characteristic fine structure and splitting patterns found in crystalline bulk spectra.\textsuperscript{193,196} From our experience with pure C\textsubscript{2}H\textsubscript{6} and mixed C\textsubscript{2}H\textsubscript{6}-CH\textsubscript{4} aerosols, we anticipated crystallization to be slower in N\textsubscript{2} than in He bath gas.\textsuperscript{183,197} The comparison of Figs. 4.4B, 4.5A.1 and B.1 for He bath gas with Figs. 4.4A, 4.5A.2 and B.2 for N\textsubscript{2} bath gas confirms this expectation. In N\textsubscript{2}, the condensates are initially formed in a disordered phase (Figs. 4.4A and 4.5A.2 at $t = 1$ s), which crystallizes over a time span of approximately 10 minutes (Fig. 4.5A.2 at $t = 627$ s), i.e. on a much longer time scale than in He ($< 1$ s).

\textsuperscript{iv}The effect of N\textsubscript{2} and He as bath gas on the crystallization of C\textsubscript{2}H\textsubscript{6} aerosols was discussed in Chapter 3.3.5.
Figure 4.4: IR spectra of (A) $n$-C$_5$H$_{12}$ aerosols in N$_2$ and (B) crystalline $n$-C$_5$H$_{12}$ aerosols in He ($n$-C$_5$H$_{12}$; bath gas = $\sim$ 10$^{-5}$:1) recorded immediately ($t = 1$ s) after injection of $n$-C$_5$H$_{12}$ gas into the cold bath gas. The cell temperature was 78 K in both cases.

The different rates of the phase transition could in principle be attributed to differences in the diffusivity of $n$-C$_5$H$_{12}$ (0.3044 cm$^2$ s$^{-1}$ in He and 0.0885 cm$^2$ s$^{-1}$ in N$_2$ at 298 K) and in the thermal conductivity of the two bath gases (75.5 mW m$^{-1}$ K$^{-1}$ for He and 9.8 mW m$^{-1}$ K$^{-1}$ for N$_2$ at 100 K). Different rates could also arise from the incorporation of N$_2$ into the $n$-C$_5$H$_{12}$ condensates. Diffusivity and thermal conductivity strongly influence the fast processes in the first few seconds during and after particle formation, which release high amounts of energy and strongly depend on the mobility of the molecules. In N$_2$, however, the crystallization of $n$-C$_5$H$_{12}$ condensates proceeds over 10 minutes at constant cell temperature – too slow for diffusion or heat conduction to play a major role. The incorporation of N$_2$ is a more plausible explanation, which would be consistent with our previous studies of the crystallization of supercooled C$_2$H$_6$ droplets in different bath gases (He, N$_2$, CH$_4$). These studies
Figure 4.5: Comparison of the temporal evolution of IR spectra of \(n\)-C\(_5\)H\(_{12}\) aerosol condensates in He (A.1 and B.1) and N\(_2\) (A.2 and B.2) (\(n\)-C\(_5\)H\(_{12}\):bath gas = \(\sim\) 10\(^{-5}\):1) at a temperature of 78 K and 800 mbar cell pressure. The two frequency ranges that are the most characteristic for the phase transition are shown. The time after the formation of the aerosol condensates is indicated for each spectrum in A.1 and A.2; in B.1 (B.2) times for the individual spectra are as for those in A.1 (A.2). The dashed lines at \(t = 49\) s in A.2 and B.2 are reconstructed spectra (see Section 4.3.2.2).

demonstrated that the incorporation of a second gas, for example CH\(_4\) or N\(_2\), into the hydrocarbon aerosols results in a depression of the particle freezing point and hence the crystallization rate. Moreover, the observed kinetics clearly correlate with the composition of such mixed droplets.\(^5\) It is expected that, while dissolved gases may be present in liquid particles and particles with a disordered solid-state structure, these gases will be expelled to a large extent during transitions to crystalline structures.\(^{205}\)

All the evidence points towards the incorporation of N\(_2\) into the \(n\)-C\(_5\)H\(_{12}\) condensates being the leading cause of the observed differences in the crystallization kinetics in N\(_2\) and in He. However, solubility data for N\(_2\) in \(n\)-C\(_5\)H\(_{12}\) are not available for the experimental conditions relevant to the present study. From recent Monte Carlo calculations,\(^5\) we know that under the same conditions liquid CH\(_4\) and C\(_2\)H\(_6\) droplets can take up substantial amounts of N\(_2\). In these cases it is clear that the initial condensates at the relevant temperatures and pressures are liquid or supercooled liquid droplets. The initial phase of the \(n\)-C\(_5\)H\(_{12}\) condensates, by
contrast, is not clear and hence we can only speculate here. The broad bands in the IR spectra (Figs. 4.4A and 4.5A.2 at $t = 1$ s) clearly hint at – at least partially – disordered phase (supercooled liquid, amorphous solid, glass or partially ordered solid), but at 65 K below the bulk melting point the survival of supercooled liquid $n$-C$_5$H$_{12}$ droplets for tens of seconds (Fig. 4.5A.2 and B.2) is rather doubtful. Note that even mixed $n$-C$_5$H$_{12}$-$N_2$ droplets with an $N_2$ content of 30% would still be supercooled by 59 K at 78 K (assuming ideal behavior and the heat of fusion of $n$-C$_5$H$_{12}$ $\Delta H_{fus} = 8.401$ kJ mol$^{-1}$ at $T = 143.47$ K).

In contrast to C$_3$H$_8$, there are no specific reports that would provide clear evidence for a particularly stable supercooled liquid phase of $n$-C$_5$H$_{12}$. An IR spectrum of solid $n$-C$_5$H$_{12}$ recorded at 78 K with similar (although not identical) broad bands to the observed aerosol spectrum was reported by Axford and Rank without any further specification of the type of solid phase (amorphous solid, glass, or partially ordered solid). The study of Takeda et al. did not detect a glass transition and indicated a low glass forming ability for $n$-C$_5$H$_{12}$. Most notably it could not confirm the glass transition at 69 K previously reported by Sugawara and Tabata which speaks against a glassy state – at least for pure $n$-C$_5$H$_{12}$. Another amorphous solid phase or partially ordered solid phase, potentially a rotator phase, appears more plausible.

Sirota et al. described the rotator phase as “typically a crystalline phase with long range positional order of the molecules in three dimensions but no long range order in the rotational degree of freedom of the molecule about its long axis.” The rotator phases of $n$-alkanes have been studied extensively for $n > 16$ ($n$ – number of C atoms) (see Sirota et al., Wentzel and Milner, and references therein), but to our knowledge studies on the rotator phase of the short-chain $n$-alkanes with $n < 9$ have not been carried out to date. The vibrational spectrum of liquid and solid $n$-C$_5$H$_{12}$ is known to depend on the conformational isomers (mainly trans-trans (TT), trans-gauche (TG), and gauche-gauche (GG)) present in the sample. Conformational isomers, or “conformers”, are isomers which arise from rotation about a single bond – in the case of $n$-C$_5$H$_{12}$ about a C-C bond. The abundance of different conformers changes with the sample temperature and with the type of phase. While the crystalline phase consists only of the lowest energy conformer TT, spectra at higher temperatures and spectra of disordered phases show contributions from the TG and GG conformers.
Figure 4.6: IR spectra of (A) liquid bulk \( n-C_5H_{12} \) at room temperature, (B) liquid \( n-C_5H_{12} \) aerosol droplets formed just above 143 K, (C) \( n-C_5H_{12} \) aerosol condensates formed immediately \((t = 1 \text{ s})\) after injection of warm \( n-C_5H_{12} \) gas into the cold cell at 78 K, and (D) crystalline \( n-C_5H_{12} \) particles at 78 K after crystallization is completed. \( N_2 \) was used as the bath gas for all aerosols.

Our \( n-C_5H_{12} \) aerosol spectra after crystallization (Figs. 4.4B, 4.5 at \( t = 625 \text{ s} \), and Fig. 4.6D) indeed show mainly contributions from the \( TT \) conformer (see also Table 4.2), while the spectra of aerosol condensates in the disordered phase (Figs. 4.4A, 4.5A.2 and B.2 at \( t = 1 \text{ s} \), and Fig. 4.6C) have additional bands from the energetically higher-lying \( TG \) conformer. Some of these bands (at 1237, 908, and 765 cm\(^{-1}\)) are indicated with arrows in Fig. 4.6C. Table 4.2 provides vibrational band positions of the crystalline and disordered aerosol condensates and compares them with literature values for solid films and liquids at different temperatures.\(^{193,211,214,216}\) The band assignments are based on the assignment provided by Keefe and Jaspers-Fayer for liquid \( n-C_5H_{12} \) at room temperature.\(^{213}\) For comparison, we have also recorded a liquid spectrum at \( T = 298 \text{ K} \) with ATR FTIR (Fig. 4.6A), which shows good agreement with the room temperature spectrum of Keefe and Jaspers-Fayer.\(^{214}\) In order to gather additional evidence to distinguish between a supercooled liquid state and a solid disordered/partially ordered state we have also recorded spectra of liquid aerosol droplets just

71
above the melting point of \( n\text{-C}_5\text{H}_{12} \) \( (T > 143 \text{ K}) \). An example is shown in Fig. 4.6B. Note that for these measurements the temperature was not uniform throughout the cell so that the temperature is specified here simply as \( T > 143 \text{ K} \). The spectra in Fig. 4.6B \( (T > 143 \text{ K}) \) and C \( (T = 78 \text{ K}) \) clearly show differing contributions from different conformers. While this could indicate a difference in phase (liquid in B vs. disordered solid in C) it could also arise from changes in the thermal population of different conformers with the phase itself unchanged.

From the above observations and arguments, we conclude that the observed reduction in the crystallization rate of \( n\text{-C}_5\text{H}_{12} \) aerosols in \( \text{N}_2 \) bath gas compared with \( \text{He} \) bath gas is probably a consequence of the incorporation of \( \text{N}_2 \) into the \( n\text{-C}_5\text{H}_{12} \) condensates upon aerosol formation. While supercooled liquid droplets cannot be completely ruled out, it seems more plausible that the condensates just after particle formation are amorphous (but not glassy) or partially ordered solids. After crystallization is complete, the IR spectra in \( \text{N}_2 \) look identical to the IR spectra of pure crystalline \( n\text{-C}_5\text{H}_{12} \) particles formed in \( \text{He} \). Therefore, the crystallization process must be accompanied by the loss of \( \text{N}_2 \) from the aerosol particles with possible implications for the kinetics which will be discussed in the following section. During crystallization dissolved gases are expelled owing to the much lower solubility of gases in crystals compared with in liquids. The process by which the \( \text{N}_2 \) is lost may be similar to that recently reported by Leisner and co-workers for freezing water droplets, whereby dissolved gas is expelled in the form of spherical bubbles, each with a volume several orders of magnitude smaller than that of the particle undergoing freezing.\(^{205} \)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{13} – S_{17}, S_{19}</td>
<td>1462(TG,TT)</td>
<td>1461</td>
<td>1464</td>
<td>1469</td>
<td>1471</td>
<td>1476,1473</td>
<td>1477</td>
<td>1474</td>
<td></td>
</tr>
<tr>
<td>S_{23}, S_{27}, S_{41}</td>
<td>1462(TG,TT)</td>
<td>1461</td>
<td>1464</td>
<td>1469</td>
<td>1471</td>
<td>1476,1473</td>
<td>1477</td>
<td>1474</td>
<td></td>
</tr>
<tr>
<td>S_{20}, S_{21}, S_{28}</td>
<td>1380(TG,TT)</td>
<td>1380</td>
<td>1379</td>
<td>1379(TG,TT)</td>
<td>1377</td>
<td>1378</td>
<td>1379</td>
<td>1379</td>
<td></td>
</tr>
<tr>
<td>S_{23}, S_{26}, S_{12}</td>
<td>1342(TG)</td>
<td>1342</td>
<td>1342</td>
<td>1342(TG)</td>
<td>1343(TG)</td>
<td>1341</td>
<td>1342</td>
<td>1336</td>
<td>1336</td>
</tr>
<tr>
<td>S_{24}, S_{29}</td>
<td>1328(TG)</td>
<td>1329</td>
<td>1306(TG)</td>
<td>1328(TT)</td>
<td>1307(TG)</td>
<td>(1306)</td>
<td>1303</td>
<td>1308</td>
<td></td>
</tr>
<tr>
<td>S_{20}, S_{24}, S_{40}</td>
<td>1306(TT)</td>
<td>1307</td>
<td>1308</td>
<td>1309(TG)</td>
<td>1294(TT)</td>
<td>1294</td>
<td>1297</td>
<td>1299</td>
<td>1299</td>
</tr>
<tr>
<td>S_{20}, S_{30}</td>
<td>1263(TT)</td>
<td>1264</td>
<td>1265</td>
<td>1263(TT)</td>
<td>1262</td>
<td>1262</td>
<td>1257</td>
<td>1258</td>
<td>1265</td>
</tr>
<tr>
<td>S_{23}, S_{27}, S_{13}</td>
<td>1238(TG)</td>
<td>1239</td>
<td>1237</td>
<td>1238(TG)</td>
<td>1237</td>
<td>1237</td>
<td>1236</td>
<td>1236</td>
<td></td>
</tr>
<tr>
<td>S_{27}, S_{28}, S_{45}</td>
<td>1164(TG)</td>
<td>1166</td>
<td>1162</td>
<td>1167(TG)</td>
<td>(1167)</td>
<td>(1168)</td>
<td>1179(TT)</td>
<td>(1180)</td>
<td>1179</td>
</tr>
<tr>
<td>S_{16}, S_{31}, S_{39}</td>
<td>1138(TT)</td>
<td>1139</td>
<td>1138</td>
<td>1139(TG)</td>
<td>1139</td>
<td>1139(sh)</td>
<td>1139</td>
<td>1138</td>
<td></td>
</tr>
<tr>
<td>S_{29}, S_{34}, S_{19}</td>
<td>1138(TG)</td>
<td>1139(TG)</td>
<td>1139(TG)</td>
<td>1075(TG)</td>
<td>1073(TG)</td>
<td>1072</td>
<td>1072</td>
<td>(1075)</td>
<td>(1067)</td>
</tr>
<tr>
<td>S_{30}</td>
<td>1073(TG)</td>
<td>1072</td>
<td>1072</td>
<td>1075(TG)</td>
<td>1067(TT)</td>
<td>1067</td>
<td>1067</td>
<td>1066,1068</td>
<td>1067</td>
</tr>
<tr>
<td>S_{15}</td>
<td>1067(TT)</td>
<td>1067</td>
<td>1067</td>
<td>1067(TT)</td>
<td>1067(TT)</td>
<td>1038(TT)</td>
<td>1037</td>
<td>1037</td>
<td>1037</td>
</tr>
<tr>
<td>S_{13}, S_{15}, S_{17}</td>
<td>1026(TT)</td>
<td>1026</td>
<td>1025</td>
<td>1027(TT,TT)</td>
<td>1026</td>
<td>1025</td>
<td>1026</td>
<td>1026</td>
<td>1025</td>
</tr>
<tr>
<td>S_{30}</td>
<td>988(TG)</td>
<td>990</td>
<td>989</td>
<td>987(TG)</td>
<td>987(TG)</td>
<td>987(TG)</td>
<td>986</td>
<td>986</td>
<td>(976)</td>
</tr>
<tr>
<td>S_{13}</td>
<td>918(TT)</td>
<td>919</td>
<td>919</td>
<td>920(TT)</td>
<td>919</td>
<td>920</td>
<td>921</td>
<td>921</td>
<td>919</td>
</tr>
<tr>
<td>S_{14}</td>
<td>908(TG)</td>
<td>908</td>
<td>908</td>
<td>908(TG)</td>
<td>908</td>
<td>908</td>
<td>908</td>
<td>908</td>
<td>908</td>
</tr>
<tr>
<td>S_{35}</td>
<td>861(TT,TT)</td>
<td>861</td>
<td>861</td>
<td>862(TG)</td>
<td>862(TG)</td>
<td>862(TG)</td>
<td>861</td>
<td>861</td>
<td>861</td>
</tr>
<tr>
<td>S_{36}</td>
<td>840(TG)</td>
<td>840</td>
<td>840</td>
<td>840(TG)</td>
<td>858(TG)</td>
<td>857</td>
<td>857</td>
<td>858,856(sh)</td>
<td>858</td>
</tr>
<tr>
<td>S_{36}, S_{37}</td>
<td>764(TG)</td>
<td>764</td>
<td>763</td>
<td>765(TG)</td>
<td>765(TG)</td>
<td>765(TG)</td>
<td>765</td>
<td>758</td>
<td>759</td>
</tr>
<tr>
<td>S_{24}, S_{39}, S_{43}</td>
<td>729(TG,TT)</td>
<td>728</td>
<td>728</td>
<td>726(TT)</td>
<td>726</td>
<td>726</td>
<td>725</td>
<td>726</td>
<td>728</td>
</tr>
</tbody>
</table>

[^a]: Keefe and Jaspers-Fayer[^213];[^b]: this work; (i): after injection, (ii): crystallized; [^c]: Axford and Rank[^211];[^d]: Snyder[^216];[^e]: Snyder and Schachtschneider[^199];[^f]: temperature gradient in cell; (sh): shoulder; (i): very weak bands, visible only at high concentrations.
4.3.2.2 Crystallization Kinetics in N\textsubscript{2} Bath Gas

Nucleation rate constants for phase transition of particles can be extracted from the analysis of time-dependent IR spectra recorded during the crystallization processes, such as those depicted in Fig. 4.5A.2 and B.2 for n-C\textsubscript{5}H\textsubscript{12} aerosols. We assumed that the usual assumptions for treating the homogeneous freezing kinetics of supercooled droplets are also valid for the crystallization of n-C\textsubscript{5}H\textsubscript{12} aerosol particles, i.e. classical nucleation theory with a first order rate equation for the phase transition of individual particles and the proper treatment of the size distribution of the particle ensemble.\textsuperscript{168} A detailed discussion of volume and surface nucleation rate constants, \(J_V(T)\) and \(J_S(T)\), respectively, is provided in Sigurbjörnsson and Signorell and references therein, and therefore here we only summarize the pertinent points of the analysis.\textsuperscript{168} The crystallization of an ensemble of particles follows the rate law:

\[
\bar{P}(t) = \frac{\int f(x,t) V(x) e^{-[J_V(T)V(x)+J_S(T)S(x)]t} dx}{\int f(x,t) V(x) dx}.
\]  

(4.1)

where \(\bar{P}(t)\) is the average volume fraction of particles at time \(t\) that are still uncrystallized. \(f(x,t)\) denotes the particle size distribution of the particle ensemble, where \(x = \ln(r/u)\) is the logarithm of the particle radius \(r\) in units of \(u = 1\) nm. \(V(x)\) and \(S(x)\) are the particle volume and the particle surface area, respectively. Eq. 4.1 considers both volume and surface contributions to nucleation, one of which usually dominates (see discussion in Sigurbjörnsson and Signorell).\textsuperscript{168} The determination of the rate constants \(J_V(T)\) and \(J_S(T)\) involved the following three steps: (i) The determination of the fraction of uncrystallized particles \(\bar{P}_{\text{exp}}(t)\) as a function of time from the experimental time dependent IR spectra, (ii) the determination of the particle size distribution \(f(x,t)\) as a function of time from the IR spectra, and (iii) the non-linear least squares fit of \(\bar{P}(t)\) to \(\bar{P}_{\text{exp}}(t)\). \(\bar{P}_{\text{exp}}(t)\) was obtained from a linear decomposition of the IR spectra into their uncrystallized and crystalline components. The first \((t = 1\) s\) and last \((t = 627\) s\) spectra in Figs. 4.5A.2 and B.2 were used as characteristic spectra for the uncrystallized and crystalline components, respectively. As an example Figs. 4.5A.2 and B.2 show the reconstructed spectrum at \(t = 49\) s (dashed line) together with the original IR spectra (full lines). It can be seen that the agreement is very good. Uncertainties in \(\bar{P}_{\text{exp}}(t)\) arising from
The reconstruction were determined by visually judging the quality of different reconstructions (see error bars in Fig. 4.7A). The particle size distribution \( f(x,t) \) was determined from the elastic light scattering in the IR spectra assuming a log-normal distribution of the particle sizes with mean particle radii \( r(t) \) and time independent geometric standard deviations \( \sigma \).\cite{4217,218}

Elastic scattering of light by particles results in slanting of the baseline of the IR extinction spectra and in an overall broadening of the absorption bands. The extent to which the baseline is slanted and the band is broadened depends on the particle size and the size distribution. \( r(t) \) and \( \sigma \) were found from linear least-squares fits of Mie simulations of the IR spectra to the experimental IR spectra.\cite{4}

Since complex refractive index data of solid \( n\)-C\(_5\)H\(_{12}\) at 78 K are currently not available our simulations instead used the complex refractive index data of bulk liquid \( n\)-C\(_5\)H\(_{12}\) at room temperature of Keefe and Jaspers-Fayer.\cite{214} To obtain an impression of the possible uncertainties arising from the use of substitute refractive indices we also performed fits with the refractive index data of solid CO\(_2\) at 12.5 and 78 K.\cite{219,220} As reported previously by Kunzmann et al., \( r(t) \) and \( \sigma \) are strongly correlated and Mie fits only allow us to determine one of them independently.\cite{218} We decided to set \( \sigma = 1.6 \), which is a typical value for aerosol particles formed in cooling cells. Additional simulations with \( \sigma = 1.2 \) and \( \sigma = 2.0 \) were carried out to estimate the uncertainty arising from this assumption.\cite{v}

Fig. 4.7B shows \( r(t) \) for a particular experiment (dots) together with a polynomial fit (line). For the various experiments we performed under slightly different conditions (concentration, pressure), mean particle radii were typically rather small, in the range from 40 to 80 nm.

The nucleation rate constants we obtained for the crystallization of \( n\)-C\(_5\)H\(_{12}\) aerosols at 78 K are

\[
J_V(T) = 10^{11} - 10^{13} \text{cm}^{-3} \text{s}^{-1} \quad (4.2)
\]

\[
J_S(T) = 10^{12} - 10^{14} \text{cm}^{-2} \text{s}^{-1} \quad (4.3)
\]

As an example Fig. 4.7A shows experimental values for \( \ln(P_{exp}(t)) \) (dots) with corresponding fits for pure volume and pure surface nucleation (solid and dashed line, respectively) for one particular measurement. The range of values given for the nucleation rate constants in Eq. 4.2

\cite{v}

A sensitivity analysis was performed regarding \( \sigma \), complex refractive index data, and integration band used for scaling and is summarized for \( n\)-C\(_4\)H\(_{10}\) in Appendix C. The same analysis was carried out for \( n\)-C\(_5\)H\(_{12}\).
and Eq. 4.3 represents the overall uncertainty including contributions from the determination of $\bar{P}_{\text{exp}}(t)$, from the Mie fits, from the use of substitute refractive index data, and from $\sigma$ as discussed above. As a result the rate constants cannot be determined more accurately than to within about one order of magnitude. Furthermore, the example in Fig. 4.7A illustrates that the quality of the data does not allow us to distinguish between surface and volume nucleation. Since this is generally the case with aerosol systems we follow the previous recommendation of Sigurbjörnsson and Signorell and report separate values for pure volume $J_V(T)$ (with $J_S(T) = 0$) and for pure surface nucleation $J_S(T)$ (with $J_V(T) = 0$). We note that the rate constants did not depend on the pressure in the cooling cells between 550 and 800 mbar nor on the $n$-C$_5$H$_{12}$ mole fractions between $3 \times 10^{-6}$ and $1 \times 10^{-4}$.

Fig. 4.7A reveals that $\bar{P}(t)$ as given by Eq. 4.1 (full and dashed lines) does not fit the experimental data (dots) very well. We found a qualitatively similar systematic deviation for all 13 of the individual $n$-C$_5$H$_{12}$ measurements we have analyzed. This is notably different from the crystallization of supercooled droplets, for example of fluoroform or of C$_2$H$_6$, which do not show such a deviation. This suggests that the crystallization of $n$-C$_5$H$_{12}$ aerosols does not obey simple homogeneous nucleation kinetics.

Weidinger et al. studied the freezing of droplets of higher $n$-alkanes ($n = 14$ to $n = 17$) using an electrodynamic balance and observed evidence for the formation of a solid surface layer before freezing of the bulk occurred. It is possible that $n$-C$_5$H$_{12}$ aerosols crystallize in a similar way, however, at 78 K the degree of supercooling ($\Delta T = 65$ K) is so high that even if a surface layer was formed first, it is expected that this process would be too fast to be observable in our experiment, and therefore this is not a likely cause for the observed deviation from the predicted crystallization behavior, which extends over about 10 minutes. As mentioned in Section 4.3.2.1, immediately after particle formation the $n$-C$_5$H$_{12}$ aerosol condensates are probably amorphous or partially ordered solid particles with some N$_2$ incorporated. In the course of the crystallization process they must expel this N$_2$ to form the pure crystalline $n$-C$_5$H$_{12}$ particles observed after crystallization is complete.

It is conceivable that the nucleation itself is influenced by the kinetics of the N$_2$ loss from the particles so that Eq. 4.1 would no longer suffice to describe the overall process.
Or, as recently observed for water droplets by Leisner and co-workers,\textsuperscript{205} individual particles may not crystallize in their entirety following nucleation, but crystallize in distinct “zones” independently within a single particle. However, this seems less likely to us because of the relatively small size of the \(n\)-C\(_5\)H\(_{12}\) particles.

### 4.3.2.3 Crystallization in the Presence of C\(_2\)H\(_2\), CO\(_2\) and H\(_2\)O

As described in Section 4.3.1.2 for C\(_3\)H\(_8\) aerosols, we also investigated the phase transition of \(n\)-C\(_5\)H\(_{12}\) aerosols in the presence of a second substance \(X = \text{C}_2\text{H}_2, \text{CO}_2, \text{or H}_2\text{O}\) for both premixed and sequential injection in an N\(_2\) bath gas at 78 K with \(n\)-C\(_5\)H\(_{12}\):\(X\) ratios between 1:1 and 4:1. Fig. 4.8 shows the \(n\)-C\(_5\)H\(_{12}\) bands in the spectral region between 1480 and 1440 cm\(^{-1}\) for premixed injection with a \(n\)-C\(_5\)H\(_{12}\):\(X\) ratio of 2:1. Compared with pure \(n\)-C\(_5\)H\(_{12}\) in N\(_2\) (Fig. 4.5A.2) the crystallization is significantly accelerated in the presence of another species with a marked dependence on the type of substance, as is to be expected for heterogeneous nucleation. C\(_2\)H\(_2\) (Fig. 4.8A) is the most effective substance, causing immediate crystallization (similar to the case of pure \(n\)-C\(_3\)H\(_{12}\) in He, Fig. 4.5A.1), while the acceleration is less dramatic for CO\(_2\) (Fig. 4.8B) and the least for H\(_2\)O (Fig. 4.8C). For C\(_2\)H\(_2\) and CO\(_2\) the temporal
behavior is independent of the $n$-$C_5H_{12}$:$X$ ratio, but in the presence of H$_2$O an increase in the crystallization rate is observed for higher H$_2$O contents. The difference between the effects of the three substances is expected to be explainable by considering their phase diagrams and their miscibility with $n$-$C_5H_{12}$. While C$_2$H$_2$ and CO$_2$ are similar in these respects, H$_2$O is rather different as it freezes at much higher temperatures and has a much lower miscibility with $n$-$C_5H_{12}$. For H$_2$O the situation could be analogous to that for C$_2$H$_6$/C$_2$H$_2$ or C$_2$H$_6$/CO$_2$ mixtures as discussed in Lang et al.\textsuperscript{197}\textsuperscript{vi}. During cooling in our cell H$_2$O probably forms solid aerosol particles before $n$-$C_5H_{12}$ starts to condense onto them as a liquid (possibly with some N$_2$ incorporated). The slight dependence of the $n$-$C_5H_{12}$ crystallization rate on the H$_2$O content would be a natural consequence of the fact that the initial H$_2$O vapor concentration determines the number concentration and size distribution of H$_2$O particles that serve as crystallization nuclei for $n$-$C_5H_{12}$. Condensation of $n$-$C_5H_{12}$ happens at temperatures between about 185 K and 220 K (i.e. above the freezing point of $n$-$C_5H_{12}$) for the $n$-$C_5H_{12}$ concentrations studied here. Further cooling below the freezing point finally leads to the crystallization of $n$-$C_5H_{12}$.

The situation for $n$-$C_5H_{12}$ mixed with C$_2$H$_2$ or CO$_2$ is different. Here liquid $n$-$C_5H_{12}$ condenses first before C$_2$H$_2$ or CO$_2$ start to condense onto the $n$-$C_5H_{12}$ droplets. For the concentrations used here condensation of C$_2$H$_2$ or CO$_2$ happens at temperatures just above or just below the melting point of $n$-$C_5H_{12}$, i.e. close to the temperature where $n$-$C_5H_{12}$ could crystallize. Similar phenomena to those observed here for $n$-$C_5H_{12}$ in the presence of C$_2$H$_2$ and CO$_2$ have previously been observed for the crystallization of supercooled C$_2$H$_6$ droplets in the presence of C$_2$H$_2$ and CO$_2$.\textsuperscript{134,183,197} As outlined in detail in Lang et al.\textsuperscript{197} the higher efficiency of C$_2$H$_2$ aerosols as heterogeneous crystallization nuclei is likely to be a consequence of the more flexible crystal structure of solid C$_2$H$_2$ compared with that of solid CO$_2$. While CO$_2$ crystallization nuclei were always found to remain in their cubic crystalline state, C$_2$H$_2$ nuclei easily adapt their structure in the presence of another substance, for example changing from ideal crystalline to polycrystalline, and thus provided a greater number, and more effective nucleation sites than crystalline CO$_2$. We believe that the same explanation also holds for $n$-$C_5H_{12}$-C$_2$H$_2$ and $n$-$C_5H_{12}$-CO$_2$, i.e. that the reason for the faster nucleation of $n$-$C_5H_{12}$ in

\textsuperscript{vi}Detailed discussion also in Chapter 3.3.3.
Figure 4.8: Time-dependent IR spectra in the region between 1440 and 1480 cm$^{-1}$ recorded during the heterogeneous crystallization of $n$-C$_5$H$_{12}$ aerosols in the presence of (A) C$_2$H$_2$ ($C_5H_{12}$:C$_2$H$_2$ = 2:1), (B) CO$_2$ ($C_5H_{12}$:CO$_2$ = 2:1), and (C) H$_2$O ($C_5H_{12}$:H$_2$O = 1.4:1). The experiments were performed in N$_2$ bath gas at a pressure of 800 mbar. The time after particle formation is indicated in panel B for each spectrum and increases from top to bottom.

The presence of C$_2$H$_2$ lies in the structural properties of the crystallization nuclei, since the differences in the condensation behavior of C$_2$H$_2$ and CO$_2$ are probably minor as pointed out above.

To test whether the sequence of the condensation of $n$-C$_5$H$_{12}$ and C$_2$H$_2$ or CO$_2$, has any significant influence on the crystallization time of $n$-C$_5$H$_{12}$, Fig. 4.9 compares premixed injection (A.1 and B.1) with sequential injection (A.2 and B.2) for the $n$-C$_5$H$_{12}$-$C_2$H$_2$ case. For the sequential injection, C$_2$H$_2$ was injected into the cell with a time delay of $\Delta t = 1$ s before $n$-C$_5$H$_{12}$ (valve opening time = 0.5 s), which ensured that the formation of solid C$_2$H$_2$ occurred before $n$-C$_5$H$_{12}$ could start to condense. The comparison of the $n$-C$_5$H$_{12}$ bands in the spectra shown in Fig. 4.9A.1 and A.2 do not indicate at a substantial dependence of the crystallization time on the sequence of the condensation. In both cases, it takes less than a few seconds for the completion of the crystallization of $n$-C$_5$H$_{12}$. The few additional seconds it takes for completion
Figure 4.9: Comparison between premixed (A.1 and B.1) and sequential injection (A.2 and B.2) for heterogeneous crystallization of \( n\text{-C}_5\text{H}_{12} \) aerosols in the presence of \( \text{C}_2\text{H}_2 \). The time-delay for the sequential injection was \( \Delta t = 1 \) s, with valve opening times of 0.5 s. Panels A.1 and A.2 show \( n\text{-C}_5\text{H}_{12} \) bands in the region between 1440 and 1480 cm\(^{-1}\). Panels B.1 and B.2 depict the region of the bending vibration of \( \text{C}_2\text{H}_2 \). The experiments were performed in \( \text{N}_2 \) bath gas at a pressure of 800 mbar. The time after particle formation is indicated in panel A.1 and B.1 for each spectrum; in A.2 (B.2) the times for the individual spectra are as for those for panel A.1 (B.1).

under conditions of sequential injection correspond to the time it takes to mix the first (\( \text{C}_2\text{H}_2 \)) and the second (\( \text{n-C}_5\text{H}_{12} \)) cloud of particles.\(^{197}\) The profile of the \( \text{C}_2\text{H}_2 \) bands depicted in Fig. 4.9B.1 and B.2 reveal that \( \text{n-C}_5\text{H}_{12} \) interacts differently with \( \text{C}_2\text{H}_2 \) or \( \text{CO}_2 \) for the two different injection routines. As observed and discussed for \( \text{C}_3\text{H}_8 \) in Section 4.3.1.2, premixed injection leads initially to the formation of crystalline \( \text{C}_2\text{H}_2 \) condensates (see triplet band structure), which convert into a less ordered structure over time. For sequential injection, less ordered \( \text{C}_2\text{H}_2 \) particles are formed initially, and as Fig. 4.9B.2 demonstrates their structure is not strongly influenced by the injection of \( \text{n-C}_5\text{H}_{12} \). The interaction between \( \text{n-C}_5\text{H}_{12} \) and \( \text{C}_2\text{H}_2 \) is apparently different for the condensates produced by the two injection schemes. Nevertheless, there are no substantial changes in the crystallization time, which takes less than a few seconds in both cases.
4.4 Conclusions

$C_3H_8$ and $n-C_5H_{12}$ aerosols are possible candidates for species involved in cloud formation on Titan. In this context their crystallization behavior plays an important role. This behavior has been studied here by rapid-scan mid-infrared spectroscopy under conditions that are representative of Titan’s lower atmosphere. It has been found that $C_3H_8$ and $n-C_5H_{12}$ aerosol condensates behave very differently under these conditions.

Despite considerable efforts, and under a range of conditions, neither crystallization nor any other phase change could be observed for $C_3H_8$ aerosols within the time scale of our experiment (several hours). The aerosol spectra did not show any dependence on the type of bath gas ($N_2$, He) or on the presence of other condensing species, such as $C_2H_2$, $CO_2$, or $H_2O$. This unusual stability against crystallization is best explained by the formation of stable supercooled viscous droplets. This explanation is also consistent with previous observations for bulk $C_3H_8$ by Snyder and Schachtschneider and with the fact that at a cell temperature of 78 K the degree of supercooling (7.5 K for pure $C_3H_8$ droplets) is relatively low.\textsuperscript{193,vii}

Even though direct observations have not been made, $C_3H_8$ is expected to condense on Titan near an altitude of about 60 km together with other substances such as $C_2H_2$, one of the main trace gases in the stratosphere.\textsuperscript{33} To simulate different condensation scenarios, we have injected $C_3H_8$ and $C_2H_2$ into our cell (i) at the same time, (ii) $C_3H_8$ followed by $C_2H_2$, and (iii) $C_2H_2$ followed by $C_3H_8$. For all cases, the $C_3H_8$ spectra were identical and showed the same features as the liquid droplet spectra mentioned above. These observations imply that $C_3H_8$ has a strong tendency to remain in the liquid state even in the presence of other compounds. With a minimum temperature of 71 K in Titan’s lower atmosphere, it is plausible that $C_3H_8$ exists mainly as a (supercooled) liquid over extended atmospheric regions and thus could substantially influence the freezing behavior of important cloud forming species, such as $CH_4$ or $C_2H_6$. Distinguishing between liquid and crystalline $C_3H_8$ on Titan in the mid-infrared region by spectroscopic means is challenging. $\nu_4$ and $\nu_5$ are the most sensitive bands, lying between 1440 and 1480 cm$^{-1}$. This region, however, coincides with strong, overlapping bands

\textsuperscript{vii}Mid-IR measurements of liquid $C_3H_8$ at 100 K as part of thin film studies confirm that the observed $C_3H_8$ aerosols are indeed liquid. A detailed discussion including the solid phases of $C_3H_8$ between 20-85 K can be found in Chapter 7.3.2.
of CH$_4$ and other hydrocarbons\textsuperscript{[188]} and suffers from a low signal-to-noise ratio\textsuperscript{[33,187]} The $\nu_{26}$ band around 748 cm$^{-1}$ would be preferable\textsuperscript{[186]} but unfortunately the spectra of liquid and solid C$_3$H$_8$ are more or less indistinguishable in this frequency range (compare Fig. 4.1A, Coustenis et al.\textsuperscript{[33]} Fig. 7, and Chapter 7 Fig 7.3).  

In contrast to C$_3$H$_8$ particles, n-C$_5$H$_{12}$ aerosol condensates crystallize quickly at 78 K. Under all of the conditions studied here crystallization was completed in less than 10 minutes. Our results provide strong indications that condensation in a N$_2$ atmosphere initially produces solid (partially) disordered mixed n-C$_5$H$_{12}$-N$_2$ particles\textsuperscript{[viii]} The ensuing crystallization process seems to be accompanied by the removal of N$_2$ from the particles. The analysis of the phase transition process with a simple nucleation model results in volume nucleation rates in the range of $J_V(T) = 10^{11} - 10^{13}$ cm$^{-3}$ s$^{-1}$ (corresponding surface nucleation rates are $J_S(T) = 10^{12} - 10^{14}$ cm$^{-2}$ s$^{-1}$). The same analysis, however, also reveals that a simple nucleation model is insufficient to describe the crystallization of the mixed n-C$_5$H$_{12}$-N$_2$ particles. Heterogeneous crystallization in the presence of other substances accelerates crystallization of n-C$_5$H$_{12}$ aerosols depending on the type of substance as expected. It is worth noting that evidence for the existence of nitrile condensates at an altitude of around 90 km has been found\textsuperscript{[222].} If transported to lower altitudes it is possible that these condensates may act as condensation and crystallization nuclei for various hydrocarbons, a process of interest for future studies.

Even though C$_5$H$_{12}$ has not yet been detected on Titan, it is a likely photochemical product that could condense in the form of aerosols. Our results suggest that solid condensates would dominate in the lower atmosphere. The IR spectra presented here reveal several spectral regions that could serve to distinguish between aerosol condensates in different phases (see for example Fig. 4.4).

\textsuperscript{viii}The initially formed phase of n-C$_5$H$_{12}$ aerosol particles in N$_2$ as bath gas at 78 K has been identified as “amorphous-annealed” by comparison to a vapor-deposited thin film of n-C$_5$H$_{12}$. Thin films of n-C$_5$H$_{12}$ and the identification of the aerosol phase are discussed in detail in Chapter 7.3.3.
Chapter 5

Infrared Spectroscopy and Phase Behavior of \( n \)-Butane Aerosols and Thin Films at Cryogenic Temperatures*

5.1 Introduction

Chapters 3 and 4 discussed the phase behavior of ethane (\( \text{C}_2\text{H}_6 \)), propane (\( \text{C}_3\text{H}_8 \)) and \( n \)-pentane (\( n\text{-C}_5\text{H}_{12} \)) aerosol particles generated in a bath gas cooling cell under atmospheric conditions relevant to Titan’s atmosphere using infrared (IR) extinction spectroscopy.

In Chapter 4 \( \text{C}_3\text{H}_8 \) and \( n\text{-C}_5\text{H}_{12} \) aerosol particles were found to have a very different phase behavior. \( \text{C}_3\text{H}_8 \) aerosols are considerably stabilized against crystallization under conditions relevant for the troposphere of Titan, remaining in a disordered phase throughout the timescale of the measurements.\(^{223}\) This is also the case in the presence of acetylene (\( \text{C}_2\text{H}_2 \)), carbon dioxide (\( \text{CO}_2 \)) and water (\( \text{H}_2\text{O} \)) aerosols, which have been shown to be effective heterogeneous crystallization nuclei for \( \text{C}_2\text{H}_6 \) and \( n\text{-C}_5\text{H}_{12} \).\(^{183,197,223}\) \( n\text{-C}_5\text{H}_{12} \) aerosols, on the other hand, undergo a phase transition from an initially disordered phase into a crystalline phase. As it is the case for \( \text{C}_2\text{H}_6 \) aerosols, the presence of a trace substance significantly accelerates the crystallization of \( n\text{-C}_5\text{H}_{12} \) aerosols and the magnitude of the effect is dependent upon the composition of the heterogeneous nuclei.\(^{223}\)

In this chapter IR spectroscopic measurements of unsupported aerosols at a temperature of 78 K targeted at understanding the phase behavior of \( n \)-butane (\( n\)-C\(_4\)H\(_{10}\)) aerosols are described. The significant difference between the behavior of C\(_3\)H\(_8\) and n-C\(_5\)H\(_{12}\) aerosols provided major motivation for these studies.\(^{223}\) By recording aerosol IR extinction spectra as a function of time the progression of the phase transitions of the aerosols was followed and the nucleation rate constants determined. The identification of the various phases of n-C\(_4\)H\(_{10}\) aerosols was achieved in conjunction with IR extinction studies on thin films of solid and liquid \( n\)-C\(_4\)H\(_{10}\).

C\(_4\)H\(_{10}\) has not yet been detected on Titan, but it is likely to be a product of Titan’s methane (CH\(_4\)) chemistry and a component of mixed hydrocarbon aerosols.\(^{88,108}\) C\(_4\)H\(_{10}\) and other substances may condense onto haze particles as they descend through the atmosphere of Titan, meaning that such composite particles may act as cloud condensation nuclei for the shorter-chain hydrocarbons.\(^{108}\)

In Section [5.3.1] the IR spectra of thin films of n-C\(_4\)H\(_{10}\) between 20 and 137 K are discussed, while Section [5.3.2] describes the identification of the observed phases of n-C\(_4\)H\(_{10}\) aerosol particles by comparison of their IR spectra with those collected from the thin films. Although useful for identifying the phases of the aerosols, thin films cannot be used as a model system for aerosols in studies of phase transition kinetics owing to the influence of the substrate. In Section [5.3.3] the determination of the nucleation rate constants for two observed phase transitions of unsupported n-C\(_4\)H\(_{10}\) aerosol particles is discussed. Section [5.3.4] is devoted to the discussion of measurements of the phase behavior of n-C\(_4\)H\(_{10}\) aerosol particles in the presence of other aerosol substances, here C\(_2\)H\(_2\), CO\(_2\) and H\(_2\)O.

### 5.2 Experimental Methods and Analysis of Phase-Transition Kinetics

#### 5.2.1 Aerosol Measurements

The experimental set-up, sample preparation and general experimental conditions for aerosol measurements using a custom-built bath gas cooling cell are described in Chapter 2.1. Specific details on the experimental conditions to study the phase behavior of n-C\(_4\)H\(_{10}\) aerosol
particles in presence and absence of the trace species C$_2$H$_2$, CO$_2$, and H$_2$O are given here for completeness.

In these measurements, the cooling cell was filled with N$_2$ gas in order to simulate the lower atmosphere of Titan. Helium (He) gas was sometimes used in place of N$_2$ in order to examine the influence of N$_2$. For the majority of the measurements the bath gas temperature was 78 K, which corresponds to that of the atmosphere of Titan at an altitude of $\sim$ 18 km or $\sim$ 60 km. These altitudes are relevant for the formation of CH$_4$ and C$_2$H$_6$ clouds, respectively.$^{22,114}$

To obtain the IR spectrum of liquid $n$-C$_4$H$_{10}$ particles, measurements were also carried out above the melting point of bulk $n$-C$_4$H$_{10}$ ($T_{fus} = 134.9$ K)$^{136}$ by using heating units to access cell temperatures above the boiling point of the cooling agent. The total gas pressure was maintained at $\sim$ 800 mbar. Pure or multicomponent aerosol particle ensembles were generated by injecting warm ($T = 293$ K) sample gases ($\sim$ 0.03-0.7% diluted in He or N$_2$) into the cell. The $n$-C$_4$H$_{10}$ mole fractions in the cooling cell during these studies ranged from $8 \times 10^{-6}$ to $7 \times 10^{-4}$. For the mixed composition aerosols, the ratios of $n$-C$_4$H$_{10}$ to CO$_2$, C$_2$H$_2$, or H$_2$O used were 4:1, 2:1 or 1:1. The time delay for sequential measurements was $\Delta t = 1.0$ s (valve opening time = 0.5 s). $n$-C$_4$H$_{10}$ was injected prior to CO$_2$, C$_2$H$_2$, or H$_2$O and vice versa.

Mid-infrared absorption spectra of the aerosol ensembles were recorded in the region from 8000 to 500 cm$^{-1}$. The spectra were recorded with a spectral resolution of 0.5 cm$^{-1}$ at time intervals of between 3 and 300 seconds, starting immediately after particle formation. The total measurement time was $\sim$ 2 hours.

### 5.2.2 Thin Film Measurements

In order to identify the evolving phase of the aerosol particles from their IR spectra, thin films of liquid and solid $n$-C$_4$H$_{10}$ were prepared and characterized at various temperatures ($20 < T < 140$ K) using IR transmission spectroscopy. The general experimental method for thin film measurements is described in Chapter 2.2 and only a brief description of the sample preparation is provided here.

Depending on the desired temperatures, the thin films were prepared either by vapor deposition onto an optical window, or by direct injection of $n$-C$_4$H$_{10}$ gas into an enclosed optical cell within which $n$-C$_4$H$_{10}$ condensed as a liquid. In order to access temperatures
between 20 and 100 K, pure $n$-$C_4H_{10}$ gas was deposited at 20 K at a rate of 10 ccm onto a ZnSe substrate under vacuum. After deposition the temperature was gradually increased to 100 K. Further heating of the vapor-deposited films above 100 K resulted in evaporation of the sample, and hence in order to obtain a spectrum of $n$-$C_4H_{10}$ near or above the melting point (134.9 K), pure $n$-$C_4H_{10}$ gas was injected into the enclosed optical cell which consists of a copper housing and ZnSe optical windows, the temperature of which was held at 140 K. The thickness of the cell was 15 mm. The temperature was then gradually lowered to 78 K and increased as required.

IR spectra of the thin films of $n$-$C_4H_{10}$ were recorded in transmission as a function of time and temperature using a FTIR spectrometer (Bruker IFS 125HR). The spectral resolution was 0.5 cm$^{-1}$ and the spectral region of interest extended from 500 to 8000 cm$^{-1}$. Each spectrum was averaged over 20 scans.

5.2.3 Kinetic Analysis of Aerosol Phase Transitions

By recording IR spectra of the aerosols as a function of time during a phase transition at constant temperature, the volume and surface nucleation rate constants, $J_V(T)$ and $J_S(T)$, can be determined, as has previously been performed for $C_2H_6$ and $n$-$C_5H_{12}$ aerosols (see also Chapter 4.3.2.2). A detailed discussion of the application of this approach to the homogenous freezing of supercooled droplets is provided in Sigurbjörnsson and Signorell. In the measurements presented here solid-solid phase transitions of aerosol particles are relevant, and it is assumed that this approach is also valid for such transitions.

The approach is based upon classical nucleation theory with a first order rate equation for the phase transition of individual particles and requires the proper treatment of the size distribution of the particle ensemble. The crystallization of an ensemble of particles follows the rate law of Eq. 4.1 as presented in Chapter 4.3.2.2 for $n$-$C_5H_{12}$.

The determination of the rate constants $J_V(T)$ and $J_S(T)$ from aerosol spectra involves the following steps: (i) The determination of the fraction of particles in the initial phase as a function of time from the experimental time dependent IR spectra ($\bar{P}_{exp}(t)$), (ii) the determination of the particle size distribution $f(x,t)$ as a function of time from the IR spectra, and (iii) the non-linear least squares fit of $\bar{P}(t)$ to $\bar{P}_{exp}(t)$. Steps (i) to (iii) were previously
described in Chapter 4.3.2.2 and can be found in detail in Appendix B. For the determination of particle size a geometric standard deviation of $\sigma = 1.6$ was chosen and the $n$-C$_4$H$_{10}$ band at $\sim 1460$ cm$^{-1}$ was used for the determination of $\bar{P}_{\text{exp}}(t)$. Since complex refractive index data of solid $n$-C$_4$H$_{10}$ at 78 K are currently not available these simulations instead used the complex refractive index data of bulk liquid $n$-C$_5$H$_{12}$ at room temperature.$^{[214]}$ In order to obtain an impression of the uncertainty arising from the use of an alternative refractive index, the simulations were also performed using complex refractive index data for solid CO$_2$ at 12.5 K.$^{[219]}$

The magnitudes of the uncertainties in the determined nucleation rate constants arising from the determination of $\bar{P}_{\text{exp}}(t)$ by linear decomposition of the aerosol spectra, determination of the size distribution from the Mie fits, the selection of $\sigma$ and the use of substitute refractive index data were discussed in detail in Lang et al. (see also Chapter 4.3.2.2 and Appendix C).$^{[223]}$ It was found that these factors limit the precision with which the nucleation rate constants can be determined to around one order of magnitude. As a consequence, for aerosol systems it is generally not possible to distinguish between surface and volume nucleation, as demonstrated by Sigurbjörnsson and Signorell,$^{[168]}$ and therefore here separate values for pure volume $J_V(T)$ (with $J_S(T) = 0$) and for pure surface nucleation $J_S(T)$ (with $J_V(T) = 0$) are reported.

## 5.3 Results and Discussion

### 5.3.1 IR Spectra of Thin Films of $n$-Butane

Solid $n$-C$_4$H$_{10}$ can exist in an amorphous phase or in one of three crystal phases – the disordered “phase I” that is stable between 107.6 K and the melting point ($T_{\text{fus}} = 134.9$ K)$^{[146]}$ or one of two phases that can exist below 107.6 K: the metastable “phase II” and the stable “phase III”.$^{[136][196]}$ $n$-C$_4$H$_{10}$ is the simplest hydrocarbon exhibiting trans-gauche isomerization, the trans conformer being the more stable form. The observation that the trans and gauche conformers of $n$-C$_4$H$_{10}$ give rise to distinct characteristic IR absorption bands can offer insights into the phase structure of the sample in question.

The IR spectra of bulk $n$-C$_4$H$_{10}$ at low temperatures have been reported on several previous occasions. Axford and Rank reported spectra, with somewhat broad peaks, for pure liquid and
solid \(n\text{-C}_4\text{H}_{10}\) at 193 and 78 K, respectively, from 1600 to 600 cm\(^{-1}\). In this work the samples were prepared by condensation of \(n\text{-C}_4\text{H}_{10}\) from the gas phase in a sample cell. The solid-state structure of the \(n\text{-C}_4\text{H}_{10}\) at 78 K was not discussed. Comerford and Gould recorded the IR spectrum of vapor-deposited samples of pure \(n\text{-C}_4\text{H}_{10}\) or \(n\text{-C}_4\text{H}_{10}\) in a matrix of solid argon from 5000 to 700 cm\(^{-1}\). The samples were deposited at either 4.2 or 20 K. It was reported that the appearance of the absorption spectrum had a pronounced dependence on temperature; heating the sample deposited at 20 K to 77 K resulted in the disappearance of certain spectral bands, and the weakening and/or shifting of others. These effects were attributed to an irreversible increase in crystallinity upon warming from 20 to 77 K. The vapor-deposited samples were reasoned to be an amorphous glass containing both the gauche and trans forms of \(n\text{-C}_4\text{H}_{10}\), while heating the sample led to reversion of the gauche form to the more stable trans form. The matrix effect was reported to be small for \(n\text{-C}_4\text{H}_{10}\), on the order of a few wavenumbers or less. Snyder and Schachtschneider measured the IR spectrum of thin films of pure \(n\text{-C}_4\text{H}_{10}\) prepared by vapor deposition. The spectrum was recorded at a temperature of 77 K from 1500 to 700 cm\(^{-1}\). The solid-state structure of the sample was not discussed. Snyder later reported the spectrum of liquid \(n\text{-C}_4\text{H}_{10}\) at 203 K. Cangeloni and Schettino reported the spectra from 4000 to 200 cm\(^{-1}\) for the three distinct crystal phases of pure \(n\text{-C}_4\text{H}_{10}\), which they described, based on the IR spectra and literature, as the disordered phase (“phase I”, 108 K), the metastable monoclinic phase (“phase II”, 77 K), and the triclinic phase (“phase III”, 77 K). The structures of these three solid phases were later determined by Refson and Pawley using neutron powder diffraction, and all three phases were shown to have a monoclinic crystal structure.

Goodman et al. reported IR spectra in the 1400-700 cm\(^{-1}\) region of \(n\text{-C}_4\text{H}_{10}\) as a vapor-deposited argon matrix at 9 K, an annealed argon matrix at 45 K, and as a pure crystalline solid at 77 K. In the reported spectra it is clear that IR absorption bands characteristic of the less stable gauche conformer of \(n\text{-C}_4\text{H}_{10}\) are only present in spectra collected from phases with “fluid” character, for example freshly-deposited amorphous or gas-phase \(n\text{-C}_4\text{H}_{10}\). Rasanen and Bondybey reported the IR spectrum of solid \(n\text{-C}_4\text{H}_{10}\) from 1500 to 700 cm\(^{-1}\) in a matrix of neon at 4 K. They studied the interconversion of the trans and gauche conformers of
Figure 5.1: IR transmission spectra collected from a thin film of $n$-C$_4$H$_{10}$ between 20 and 137 K. Spectra A to D were obtained from a vapor-deposited sample on a ZnSe substrate. Spectra E to G were obtained from a sample of $n$-C$_4$H$_{10}$ contained within a closed cell. The spectra in the rightmost three panels have been scaled as indicated for clarity. All spectra are baseline corrected.

$n$-C$_4$H$_{10}$ initiated by IR irradiation.

While these previously-reported spectra offer many insights for identifying the evolving phase of the aerosol particles in our measurements, for certain phases of the aerosols a counterpart in the literature under comparable conditions is not available, and therefore pure thin films of liquid and solid $n$-C$_4$H$_{10}$ were prepared and characterized using IR spectroscopy over the spectral region from 8000 to 500 cm$^{-1}$ between 20 and 137 K. The collected spectra are presented in Fig. 5.1 for selected spectral regions and temperatures. These spectra are expected to be of use as a reference for future studies of solid and liquid $n$-C$_4$H$_{10}$ in planetary and lunar atmospheres.

The spectra shown in Fig. 5.1 parts A to D were recorded during the heating of a vapor-
deposited film of pure \( n\text{-C}_4\text{H}_{10} \) (deposition at 20 K). The spectra shown in Fig. 5.1 parts G to E were obtained from a directly-injected initially liquid sample of \( n\text{-C}_4\text{H}_{10} \) contained in the optical cell described in Section 5.2.2. The initial sample was injected into the cell at 140 K and then cooled down to 78 K. The observed band positions for the spectra presented in Fig. 5.1 are summarized in Table 5.4. Each of the spectra A to G is characteristic of a distinct phase of \( n\text{-C}_4\text{H}_{10} \); the preparation and spectrum of each of these phases will be discussed in turn in the sections that follow.

5.3.1.1 Amorphous \( n\text{-Butane} \)

It should be noted that thin film measurements at around 78 K, the temperature in our cooling cell, are not sufficient to capture all of the phases observed in our aerosol measurements. This is because the aerosols do not reach the thermodynamically-favored phase immediately after formation. For example, compared with all of the previously-reported spectra, the spectrum of the aerosol particles immediately after formation at 78 K was most similar to that recorded by Goodman et al. from a thin film of \( n\text{-C}_4\text{H}_{10} \) which had been annealed by heating to 45 K.\(^{196}\)

The spectrum measured by Goodman et al. was, however, that of \( n\text{-C}_4\text{H}_{10} \) in a matrix of argon, which is expected to lead to spectral shifts, albeit small ones, compared with a spectrum of pure \( n\text{-C}_4\text{H}_{10} \).\(^{195}\) An annealed thin film of pure \( n\text{-C}_4\text{H}_{10} \) was therefore prepared for comparison with the aerosol spectrum immediately after particle formation. Pure \( n\text{-C}_4\text{H}_{10} \) was deposited at 20 K and the IR spectrum of the freshly-deposited sample recorded (Fig. 5.1A). Vapor deposition at 20 K is expected to lead to the preparation of an amorphous solid-state structure,\(^{195}\) and hence we refer to this phase of \( n\text{-C}_4\text{H}_{10} \) as “amorphous” hereafter. Freshly vapor-deposited samples contain a mixture of isomers similar to that present in the gas phase, and hence this preparation method offers a means to “trap” unstable conformers in the solid state;\(^{195,196}\) both the \textit{trans} and \textit{gauche} forms of \( n\text{-C}_4\text{H}_{10} \) are represented in the spectrum shown in Fig. 5.1A (see Table 5.4 for assignments of the bands to each conformer).

Comparing the pure amorphous \( n\text{-C}_4\text{H}_{10} \) spectrum recorded here at 20 K to the amorphous matrix probed by Goodman et al. at 9 K, all bands are shifted by up to 4 cm\(^{-1} \) in frequency, and several additional bands are observed. The spectral differences are attributed to the presence of the matrix in the Goodman et al. study and the difference in temperature between the two
measurements.

Following the method of Goodman et al., the vapor-deposited film was heated to 45 K, and held at this temperature for 45 minutes. The resulting phase is referred to as “amorphous-annealed” hereafter. The spectrum of the amorphous-annealed pure n-C$_4$H$_{10}$ shown in Fig. 5.1B is that recorded while the sample was held at 45 K. At 45 K the bands at 747, 789, 955, 1076, 1132, 1169, 1258, 1338, and 1344 cm$^{-1}$ were observed to disappear or to reduce dramatically in intensity. As in the study of Goodman et al., the bands that disappear upon heating have been attributed to the less stable gauche conformers of n-C$_4$H$_{10}$ (see Table 5.4). The amorphous-annealed phase can therefore be described as an amorphous phase but with a lower fraction of gauche conformers than are present in the gas phase.

5.3.1.2 Crystalline n-Butane

The amorphous-annealed n-C$_4$H$_{10}$ film was heated above 45 K in order to collect IR spectra from crystalline n-C$_4$H$_{10}$. When a temperature of 60 K was reached the spectrum collected from the film started to change, indicating the onset of crystallization. At $T = 67$ K a dramatic change in the IR spectrum was observed; the resulting spectrum is shown as Fig. 5.1C. By comparing this spectrum with those reported for the three known crystalline forms of n-C$_4$H$_{10}$ by Cangeloni and Schettino, it can be seen that this spectrum displays bands characteristic of phases II and III, as well as number of bands that were not observed for phases I, II or III: the bands found at 947, 985, 1287, 1370, 1374, 1460, and 1461 cm$^{-1}$. It has not been possible to assign these bands, but since all bands are rather sharp this spectrum is assumed to have been collected from what is referred to here as a mixed crystal phase.

As the temperature was increased above 67 K the contributions to the IR spectrum from bands attributed to phases II and III increased and the intensity of the unassigned bands decreased. At 85 K a rapid change in the spectrum was observed (Fig. 5.1D), consistent with transformation of the n-C$_4$H$_{10}$ into phase III.

In order to prepare a film of the metastable solid phase II, it is necessary to rapidly cool a sample of liquid or phase I n-C$_4$H$_{10}$. The spectra shown in Fig. 5.1 parts G, F and E document this process. Fig. 5.1G shows the spectrum of liquid n-C$_4$H$_{10}$ at 137 K, which was prepared by direct injection of n-C$_4$H$_{10}$ gas into the optical cell described in Section 5.2.2. Upon cooling
the \( n\text{-C}_4\text{H}_{10} \) existed as a supercooled liquid until it reached a temperature of around 130 K, at which point the \( n\text{-C}_4\text{H}_{10} \) underwent a transition to the disordered phase I. Upon further cooling transition to phase II was observed at a temperature of 90 K; the spectrum collected from phase II \( n\text{-C}_4\text{H}_{10} \) at a temperature of 83 K is shown as Fig. 5.1E. It was not possible to obtain a spectrum of pure phase II \( n\text{-C}_4\text{H}_{10} \) at 78 K as at this temperature transformation into phase III has begun. Upon reheating the sample is transformed back into phase I at a temperature of 107 K, consistent with the solid-solid transition temperature of 107.6 K reported by Aston and Messerly.\(^{146}\)

### 5.3.1.3 Liquid \( n\text{-Butane} \)

As discussed in Section 5.3.1 above, IR spectra of liquid \( n\text{-C}_4\text{H}_{10} \) have previously been reported by Axford and Rank and Snyder at 193 and 203 K, respectively.\(^{216,224}\) To our knowledge an IR spectrum of liquid \( n\text{-C}_4\text{H}_{10} \) close to the melting point (134.9 K) has not been reported. The liquid spectrum collected at 137 K in these measurements is shown in Fig. 5.1G. The bands are significantly narrowed compared to those in the spectra reported by Axford and Rank and by Snyder. As expected, similar peaks were observed in the spectrum from the liquid (Fig. 5.1G) and the spectrum collected from the freshly vapor-deposited solid (Fig. 5.1A), indicating that the vapor-deposited solid might be composed of a mixture of isomers that resembles the composition of the liquid phase.

### 5.3.2 Identification of the Phases of the Aerosol Particles

After formation in the cooling cell at 78 K, \( n\text{-C}_4\text{H}_{10} \) aerosol particles were observed to undergo two phase transitions. It was therefore necessary to identify three phases of the \( n\text{-C}_4\text{H}_{10} \) aerosols: (i) that of the particles immediately after formation, (ii) that at the completion of the first phase transition and (iii) that at the completion of the second phase transition. The identification was carried out by comparing the IR spectra obtained from thin film measurements of \( n\text{-C}_4\text{H}_{10} \) (see Fig. 5.1) with those collected from the aerosol particles. For the aerosol particles studied here, the IR absorption spectrum will not be strongly influenced by the particle size and shape, and hence comparison with spectra collected from thin films is justified.\(^{227}\)
Figure 5.2: A comparison of the spectrum of (A) \( n-C_4H_{10} \) aerosol particles collected immediately after particle formation at 78 K with the spectra of a thin film of (B) amorphous-annealed \( n-C_4H_{10} \) at 45 K, (C) amorphous \( n-C_4H_{10} \) at 20 K, and (D) liquid \( n-C_4H_{10} \) at 137 K.

5.3.2.1 Phase of \( n \)-Butane Aerosols Immediately after Formation

In previous cooling cell measurements, injection of \( C_2H_6 \) or \( C_3H_8 \) into the cold bath gas led to the formation of supercooled liquid droplets.\[111,168,183,197,223\] \( n-C_4H_{10} \), however, has a melting point of 134.9 K, some 45-50 K higher than that of \( C_2H_6 \) or \( C_3H_8 \) (\( T_{fus} = 89.9 \) K or 85 K, respectively),\[167,191\] and hence it is likely that the aerosol particles condense directly to the solid state upon introduction of \( n-C_4H_{10} \) gas into the cell when at 78 K. That the particles are solid immediately after injection of gas to the cell is supported by the observation that the bands in the earliest spectrum after gas injection, shown in Fig. 5.2A, match closely with that recorded for a thin film of solid, amorphous-annealed, \( n-C_4H_{10} \) (Fig. 5.2B). In particular the band at 1133 cm\(^{-1}\) which is prominent in the spectrum of fluid \( n-C_4H_{10} \) is missing.\[224\]

To confirm that the spectrum shown in Fig. 5.2A is not characteristic of liquid \( n-C_4H_{10} \) aerosols, spectra were collected from aerosol particles formed in the cooling cell at a temperature above the melting point of bulk \( n-C_4H_{10} \). The collected aerosol spectrum is compared
with that of a thin film of liquid $n$-$C_4H_{10}$ in Fig. 5.3. It can be seen that the spectra match closely and the band at 1133 cm$^{-1}$ which is prominent in the spectrum of fluid $n$-$C_4H_{10}$ is present in this aerosol spectrum, supporting our finding that after formation at 78 K the $n$-$C_4H_{10}$ aerosols were not in a supercooled liquid state. However, a number of bands present in the liquid thin film spectrum either have a lower intensity (788, 1133, and 1339 cm$^{-1}$) or are not visible (804, 1076, 1150, and 1281 cm$^{-1}$) in the liquid aerosol spectrum. These bands, except for those at 804 and 1150 cm$^{-1}$, have been found to be characteristic of the less stable gauche conformer of $n$-$C_4H_{10}$. This suggests that for the spectrum shown in Fig. 5.3A all of the aerosols in the cell were not in fact liquid, but that some particles were present in the amorphous-annealed phase. Note that for these measurements it was not possible to maintain a uniform temperature throughout the cell; the temperatures at the bottom, middle and top of the cell were 105, 146 and 164 K, respectively. Although immediately after formation the particles are expected to be present in the upper part of the cell, where the temperature is above the melting point of $n$-$C_4H_{10}$, it is possible that there is also a small contribution from particles which have travelled to the lower, colder parts of the cell, which may be solid. This would explain the differences in the spectra.

A further difference between the spectra shown in Fig. 5.3 is the occurrence of a peak at 661 cm$^{-1}$ in the thin film spectrum. This peak is not observed in the spectra of liquid aerosols or the spectra of liquid $n$-$C_4H_{10}$ reported by Axford and Rank and Snyder. This peak was however also observed in spectra collected from thin films of liquid $C_2H_6$.

As mentioned above, the spectra demonstrate that the $n$-$C_4H_{10}$ aerosols are in the amorphous-annealed phase immediately following formation (Fig. 5.2B). It is expected that the particles are formed in the amorphous-annealed structure, rather than an amorphous phase, because the temperature in the cell under these conditions is too high for the isomeric composition of the gas phase to be “trapped”, and instead a proportion of the gauche conformers are able to convert into the more stable trans form. The aerosol spectrum was observed to be the same following formation regardless of whether $N_2$ or He was used as the cell bath gas, suggesting that $N_2$ is not incorporated into the aerosol particles of $n$-$C_4H_{10}$. This is in contrast to the behavior of $C_2H_6$ and $n$-$C_5H_{12}$ aerosols.
Figure 5.3: A comparison of the spectrum of liquid $n$-$C_4H_{10}$ aerosol particles at $T > 135$ K (A) with the spectrum of a thin film of liquid $n$-$C_4H_{10}$ at $T = 137$ K (B).

5.3.2.2 Phase of $n$-Butane Aerosols after the First Transition

Fig. 5.4 compares the IR spectrum of $n$-$C_4H_{10}$ aerosol particles at 78 K after completion of the first observed phase transition (part A) with that collected from a thin film of solid $n$-$C_4H_{10}$ in phase II at 83 K (part B). The two spectra are in good agreement, and hence it is concluded that the first observed phase transition of $n$-$C_4H_{10}$ aerosols is from the initial amorphous-annealed phase into the crystalline phase II. As described by Cangeloni and Schettino, in the spectrum characteristic of phase II all bands appear as doublets apart from those that are combination bands, or those for which the splitting is too small to be observed.\textsuperscript{136} The agreement between the observed spectrum and that of the pure $n$-$C_4H_{10}$ thin film is another strong hint that large amounts of $N_2$ are not incorporated into the particle. The agreement also suggests that the particles are completely crystalline, and not partially-amorphous or polycrystalline as is sometimes the case for aerosol particles under conditions relevant for Titan.\textsuperscript{161}
Figure 5.4: A comparison of the spectrum of \textit{n}-\textit{C}_4\textit{H}_{10} aerosol particles after completion of the first observed phase transition at \( T = 78 \) K (A) with the spectrum of a thin film of \textit{n}-\textit{C}_4\textit{H}_{10} in phase II at \( T = 83 \) K (B).

Figure 5.5: A comparison of the spectrum of \textit{n}-\textit{C}_4\textit{H}_{10} aerosol particles after completion of the second observed phase transition at \( T = 78 \) K (A) with the spectrum of a thin film of \textit{n}-\textit{C}_4\textit{H}_{10} in phase III at \( T = 85 \) K (B).
5.3.2.3 Phase of n-Butane Aerosols after the Second Transition

Fig. 5.5 compares the IR spectrum of $n$-C$_4$H$_{10}$ aerosol particles at 78 K after completion of the second observed phase transition (part A) with that collected from a thin film of solid $n$-C$_4$H$_{10}$ in phase III at 78 K (part B). The two spectra are in good agreement, and hence it is concluded that the second phase transition of $n$-C$_4$H$_{10}$ aerosols that is observed is from the crystalline phase II into phase III.

5.3.3 Phase Transitions of Pure n-Butane Aerosols

The two observed phase transitions of $n$-C$_4$H$_{10}$ aerosol particles will now be discussed in more detail.

5.3.3.1 Phase Transition from Amorphous-Annealed to Phase II

As discussed in Section 5.3.2, the first transition is that from the amorphous-annealed phase to the metastable crystalline phase II. Fig. 5.6 shows the time evolution of the first transition in a bath gas of N$_2$ (part A) or He (part B). The bands shown are those for which the band shape is most sensitive to the phase of the particles. This phase transition is completed within around 120 s. By comparing Fig. 5.6A and Fig. 5.6B, it can be seen that the transition takes a similar amount of time regardless of the bath gas. At first glance this is somewhat surprising because in previous studies it was observed that changing the bath gas from N$_2$ to He had a significant effect on the timescale of the phase transition, for example the crystallization of supercooled C$_2$H$_6$ aerosol particles was observed to be faster in He than in N$_2$.\textsuperscript{183,197} This effect was attributed to the incorporation of N$_2$ (but not He) into the supercooled droplets, resulting in a depression of the particle freezing point, a lowering of the degree of supercooling and hence a reduction in the rate of crystallization. The crystallization of amorphous n-C$_5$H$_{12}$ aerosol particles was also faster in He than in N$_2$.\textsuperscript{223} In this case the effect was also attributed to the incorporation of N$_2$ into the initially-formed amorphous particles. In the case of n-C$_5$H$_{12}$ crystallization in He was so fast that rate constants for the phase transitions could not be determined, meaning that a quantitative comparison with those determined when N$_2$ was used as the bath gas was not possible. The absence of a dependence on the bath gas for n-C$_4$H$_{10}$ suggests that N$_2$ is not incorporated into the initially-formed amorphous particles.
Figure 5.6: Time evolution of the IR spectrum of $n$-C$_4$H$_{10}$ aerosol particles during the first observed phase transition at $T = 78$ K in N$_2$ (A) and He (B). The bands shown are those that are the most sensitive to the phase of the particles. The time after particle formation is indicated for each spectrum in the leftmost frame and is the same for the adjacent frames.
In the case of n-C₄H₁₀ aerosols it has been possible to determine the rate constants for pure volume and pure surface nucleation, $J_V$ and $J_S$, respectively, for the first phase transition of n-C₄H₁₀ aerosol particles in both He and N₂. The rate constants were determined to be $J_V = 10^{12} - 10^{14}$ cm⁻³ s⁻¹ and $J_S = 10^{13} - 10^{15}$ cm⁻² s⁻¹, independent of the bath gas. In this case not only the rate constants, but also the crystallization times, were independent of the bath gas (note that even if the crystallization times are different, the rate constants can be the same, for instance if particles with different sizes are formed in the two different bath gases). Fig. 5.7 shows the typical time dependence of the mean particle size in N₂ and He. It can be seen that during the first $\sim 120$ s of a measurement, the time period relevant for the completion of the first observed phase transition, the mean particle size does not depend on the bath gas. In the absence of a significant difference in the particle size distribution, which is expected to be the case, the lack of dependence of both the crystallization time and the rate constant on the bath gas, along with confirmation that the mean particle size is not significantly different, indicates that significant amounts of N₂ are not incorporated into n-C₄H₁₀ aerosols under these conditions, in agreement with our findings from the shape of the aerosol spectra which were outlined in Section 5.3.2.1. Fig. 5.7 also reveals that the particle distributions evolve differently after 120 s in N₂ and He. The mean radii are greater in N₂, i.e. the particles grow faster in N₂ than in He. This growth happens because smaller particles have a higher vapor pressure than larger particles. As a consequence larger particles grow at the expense of smaller particles and the mean size increases over time. The average size in He is probably smaller because n-C₄H₁₀ vapor is lost to the walls more efficiently in He than in N₂. Please note again that the region beyond 120 s is not of interest for the first phase transition itself.

Fig. 5.8A shows the experimental values for $\ln(P_{exp}(t))$ as a function of time during the first phase transition for one particular measurement in N₂. The data are accompanied by the corresponding fits for pure volume and pure surface nucleation. It can be seen that the fits, which are based upon Eq. 4.1, do not closely represent the experimental observations. The same deviation is observed for this phase transition of n-C₄H₁₀ aerosols in He, and to a lesser extent a similar deviation was also observed in the case of the crystallization of n-C₅H₁₂ aerosol
Figure 5.7: Typical time evolution of the mean particle radius $r(t)$ in He (open circles) and $N_2$ (closed circles).

Figure 5.8: Logarithm of the fraction of particles that remain in the initial phase as a function of time $ln(\bar{P}_{\exp}(t))$ for the first (A) and second (B) observed phase transitions. Closed circles with error bars: Experimental data, solid line: Fit for pure volume nucleation ($J_S(T) = 0$), dashed line: Fit for pure surface nucleation ($J_V(T) = 0$). The two fits were calculated using $\sigma = 1.6$. In part B $t = 0$ s is equivalent to a time of 120 s after particle formation. Please note that the magnitude of the negative error bar shown has been reduced by using symmetric error bars for a total of three data points ($t = \sim 95$ s in A and $t = \sim 3600$ s and $\sim 5000$ s in B) for clarity.
particles in N₂. This suggests that the phase transition from the amorphous-annealed phase to phase II for n-C₄H₁₀ aerosols does not obey simple, first order homogeneous nucleation kinetics. It may be the case that the phase transition instead proceeds via a two-step process, first involving the formation of a crystalline surface layer followed by crystallization of the bulk, as previously described by Weidinger et al., and recently demonstrated by Wyslouzil and co-workers for n-octane and n-nonane. Or, as recently observed for H₂O droplets by Leisner and co-workers, individual particles may not crystallize in their entirety following nucleation, but rather crystallize in distinct zones independently within a single particle. It is possible that at the start of the phase transition the n-C₄H₁₀ aerosol particles are not uniformly annealed, which would be likely to promote such a “zonal” crystallization process.

5.3.3.2 Phase Transition from Phase II to Phase III

As discussed in Section 5.3.2, the second transition is an inter-crystal transformation from n-C₄H₁₀ in the metastable phase II to phase III. Fig. 9 shows the time evolution of the second transition in a bath gas of N₂ (part A) or He (part B). This phase transition is completed within around 5000 s. The pure volume and pure surface nucleation rate constants for the transition from phase II to phase III were found to be $J_V = 10^9 - 10^{11}$ cm$^{-3}$ s$^{-1}$ and $J_S = 10^{11} - 10^{13}$ cm$^{-2}$ s$^{-1}$, again independent of the bath gas. Fig. 5.8B shows the experimental values for $\ln(P_{exp}(t))$ as a function of time during the second phase transition for one particular measurement in N₂. The data are accompanied by the corresponding fits for pure volume and pure surface nucleation. In contrast to the first observed phase transition (Fig. 5.8A), the quality of the fit between the experimental data and the simulations indicate that the transition from phase II to phase III follows simple homogeneous nucleation kinetics.

Although in previous studies of hydrocarbon aerosols phase transitions were generally observed to proceed significantly faster in He than N₂, it is perhaps not surprising that for a crystal-crystal phase transition the bath gas does not significantly influence the rate constant. It is the incorporation of N₂, but not He, which usually gives rise to the difference in the rate of the phase transitions of hydrocarbon aerosols. In the case of a transition from an initially crystalline state, however, incorporation of the bath gas is not expected to play a role as any dissolved gases are expected to have been expelled during crystallization. Indeed,
Figure 5.9: Time evolution of the IR spectrum of $n$-C$_4$H$_{10}$ aerosol particles during the second observed phase transition at $T = 78$ K in N$_2$ (A) and He (B). The bands shown are those that are the most sensitive to the phase of the particles. The time after the start of the phase transition is indicated for each spectrum in the leftmost frame and is the same for the adjacent frames. The time after particle formation is shown in parenthesis for the first spectrum in each part.
the appearance of the observed aerosol spectra suggests that significant amounts of N$_2$ are not incorporated into the particles (see Section 5.3.2.2).

By comparing Fig. 9A and B, it can be seen that although the rate constants are independent of the bath gas, the transition is completed sooner when N$_2$ is the bath gas. Indeed, in He the transition to phase III is not completed on the timescale of these measurements. This difference in the timescale of the phase transitions is likely to be the result of differences in particle size in the two bath gases. As Fig. 5.7 shows, the mean size of particles is larger in N$_2$ than in He as the second phase transition proceeds (120 s in Fig. 5.7 = 1 s in Fig. 5.9). Larger particles recrystallize faster even if the rate constant is the same (see Eq. 4.1). Differences in the thermophysical properties of the two bath gases leads to different particle size evolutions over the measurement timescale, as shown in Fig. 5.7. As mentioned in Section 5.3.3.1, on a timescale of 1000 s of seconds, which is relevant for the second phase transition, particle growth is more efficient in N$_2$ than in He, and hence the crystallization time is shorter. A rough calculation assuming pure volume nucleation suggests that the difference in the mean particle sizes is of the correct order of magnitude to account for the difference in the crystallization time.

5.3.4 Phase Transitions of Mixed Aerosol Systems: n-Butane Mixed with C$_2$H$_2$, CO$_2$, or H$_2$O

A wide range of trace species which could condense to form aerosols, possibly at altitudes similar to those at which C$_4$H$_{10}$ could condense, including C$_2$H$_2$ and CO$_2$, are present in the lower atmosphere of Titan. Such aerosols could play an important role as heterogeneous condensation and crystallization nuclei in the formation and evolution of hydrocarbon clouds on Titan, and it has previously been demonstrated in laboratory studies that in the presence of aerosols of C$_2$H$_2$ or CO$_2$ the rate of crystallization of C$_2$H$_6$ increases significantly. The same effect has also been observed for n-C$_3$H$_{12}$ aerosol particles in the presence of C$_2$H$_2$, CO$_2$, or H$_2$O aerosols.

In this study the effect of the presence of a second aerosol substance was examined for the two observed phase transitions of n-C$_4$H$_{10}$ aerosols. The n-C$_4$H$_{10}$ aerosols were exposed to C$_2$H$_2$, CO$_2$, or H$_2$O aerosol particles using two distinct approaches. In the first approach the trace gas was premixed with the n-C$_4$H$_{10}$ gas prior to injection into the cell. In this case
either the trace substance condenses and freezes immediately after injection and \( n-C_4H_{10} \) gas later condenses onto the frozen nuclei (in the case of \( H_2O \)), or \( n-C_4H_{10} \) condenses followed by the trace species (in the case of \( C_2H_2 \) and \( CO_2 \)), giving rise to a core-shell or partially-coated particle structure. This approach is therefore expected to simulate an immersion freezing mechanism. In the second approach, the trace substance and \( n-C_4H_{10} \) gas are injected separately through two individual valves. Simultaneous injection of the two gases through the two inlet tubes is equivalent to the first approach and also mimics immersion freezing. However, if a time delay between the injections of the two gases is introduced (sequential injection), the condensed particles of the trace substance will have time to diffuse away from the region of the cell where gases are injected, and pure \( n-C_4H_{10} \) droplets will condense. It is therefore expected that as the time delay is increased a contact freezing mechanism will begin to dominate.

As discussed in detail by [Lang et al.](#) and in Chapter [3.3.3](#), proof of interaction between the aerosols of the trace substances and those of \( n-C_4H_{10} \) is provided by both the observed effects on the phase transition kinetics, and by the observed appearance of the \( \nu_5 \) band of \( C_2H_2 \) in these measurements. Pure \( C_2H_2 \) aerosols formed under these experimental conditions are known to crystallize in a partially disordered (or possibly polycrystalline) structure, for which a broad unstructured \( \nu_5 \) band is characteristic. In the presence of a second condensing gas, however, this band appears as a triplet with maxima at 736, 772, and 787 cm\(^{-1}\), which is characteristic of crystalline orthorhombic aerosol particles, which then gradually reverts to an unstructured profile over time. It is thought that the condensation of the second gas, here \( n-C_4H_{10} \), provides the necessary energy required for structural rearrangement of \( C_2H_2 \) from a partially-disordered to a crystalline form.

The size distribution of the aerosols of the trace species is not well known for these measurements because the particles are too small (\(< 100 \text{ nm in diameter}\)) to produce a scattering signature suitable for precise comparison with Mie theory. The rate of heterogeneous nucleation depends strongly on the nuclei size distribution, and hence the rate constants for the heterogeneously nucleated phase transitions of \( n-C_4H_{10} \) droplets cannot be accurately determined from these measurements. Even though a quantitative analysis cannot be provided, qualitative freezing results are presented in the sections that follow.
Figure 5.10: Time evolution of the IR spectrum of \( n-C_4H_{10} \) aerosol particles during the first (A.1 and A.2) and second (B.1 and B.2) observed phase transition at \( T = 78 \) K in \( N_2 \), for pure \( n-C_4H_{10} \) particles (A.1 and B.1) and mixed \( n-C_4H_{10}/CO_2 \) particles prepared using pre-mixed injection (A.2 and B.2). The time after the start of the phase transition is indicated for each spectrum and the time after particle formation is shown in parenthesis for the first spectrum in B.1 and B.2.

### 5.3.4.1 First Phase Transition

As was observed in previous studies of hydrocarbon aerosols,\cite{183,197,223} crystallization of \( n-C_4H_{10} \) was significantly accelerated in the presence of heterogeneous nuclei. Indeed, amorphous-annealed \( n-C_4H_{10} \) aerosols crystallized in less than 15 seconds in the presence of aerosols of \( C_2H_2 \), \( CO_2 \) or \( H_2O \), whereas homogeneous crystallization from the amorphous-annealed phase to phase II took around 120 seconds (see Figs. 5.10A.2. and 5.10A.1). This was the case whether \( N_2 \) or \( He \) was used as the bath gas.

In previous measurements the rate of heterogeneous crystallization has been found to depend on the composition of the trace nuclei. In the case of supercooled \( C_2H_6 \) droplets, \( C_2H_2 \) aerosols were found to be more effective ice nuclei than \( CO_2 \) particles, attributed to the fact that they have a less ordered surface structure than \( CO_2 \) particles.\cite{197,223} In the case of crystallization of solid amorphous \( n-C_5H_{12} \), the effectiveness of the aerosols of the trace substances, from most to least effective, was as follows: \( C_2H_2 > CO_2 > H_2O \).\cite{223} The dependence was explained by considering both the surface structure of the trace nuclei and their number concentration.
and size distributions. In terms of the role of nucleation mechanism, for $C_2H_6$ immersion freezing was found to be more efficient than contact freezing under the experimental conditions, while for $n$-$C_5H_{12}$ a dependence on nucleation mechanism was not observed. As was the case for $n$-$C_5H_{12}$ and $C_2H_6$, we find that the first observed phase transition of $n$-$C_4H_{10}$ is also accelerated most significantly by $C_2H_2$ and CO$_2$ aerosols, and to a lesser extent by H$_2$O aerosols. As was the case for $n$-$C_5H_{12}$, a dependence on nucleation mechanism was not observed. Overall, the behavior we find here for $n$-$C_4H_{10}$ is consistent with that for $n$-$C_5H_{12}$. This might be a consequence of the fact that in both cases a solid-solid phase transition from an amorphous to a crystalline phase is involved. Tentative explanations for these observations were provided by Lang et al. (Chapter 4).

### 5.3.4.2 Second Phase Transition

The second observed phase transition of $n$-$C_4H_{10}$ aerosols is a crystal-crystal transformation, from phase II to phase III, rather than a process of crystallization from a disordered phase, and hence comparisons with previous work should be drawn with care. Furthermore, as this transition commences many seconds after the formation of the aerosols in the cell, the fate of the trace nuclei must be considered carefully. It is clear from the observed acceleration of the first phase transition (Fig. 5.10) that a significant number of the trace substance aerosols have been in physical contact to the $n$-$C_4H_{10}$ aerosols by the time the second phase transition begins.

In contrast to all previous measurements, the transition of $n$-$C_4H_{10}$ aerosols from phase II to phase III was observed to proceed more slowly in the presence of a second substance in the aerosol phase (see Fig. 5.10B.1 and B.2). For the same concentration of $n$-$C_4H_{10}$ in the cooling cell, and with a N$_2$ bath gas, it takes around 10 minutes for half of the $n$-$C_4H_{10}$ aerosols to convert to phase III in the absence of a second substance, but around 90 minutes in the presence of CO$_2$ in the aerosol phase. This effect is more pronounced the greater the amount of CO$_2$ introduced to the cell. It might be expected that this effect, which was observed regardless of whether the second aerosol substance was $C_2H_2$, CO$_2$, or H$_2$O, is the result of the presence of a volume of CO$_2$ included within or at the surface of the $n$-$C_4H_{10}$ particles disturbing the growth of the crystalline phase III. However, the difference between the rates of
mean particle radius $r(t)$ in $N_2$ (closed circles) and He (open circles) for mixed $n$-$C_4H_{10}/CO_2$ aerosol particles ($n$-$C_4H_{10}$:CO$_2$ = 4:1).

The homogeneous and heterogeneous phase transitions could also arise simply from a difference in the size of the $n$-$C_4H_{10}$ part of the particles. Fig. 5.11 shows the evolution of the mean particle radius over the measurement timescale in the presence of CO$_2$ in the aerosol phase. The particles were assumed to be composed of pure $n$-$C_4H_{10}$ for the purposes of the size determination. By comparing Figs. 5.7 and 5.11 it can be seen that during the second phase transition the particles are smaller in the heterogeneous measurement. In addition, in the case of the mixed aerosols some of the particle volume is taken up by CO$_2$, and hence the volume (or surface area) within which nucleation of the $n$-$C_4H_{10}$ crystal transformation can occur is lower in the case of the mixed particles and hence the phase transition time is longer than in the homogeneous case. A rough calculation assuming pure volume nucleation suggests that if the effective radius of the $n$-$C_4H_{10}$ part of the particle is around half of that in the case of the pure $n$-$C_4H_{10}$ aerosols then this could account for the difference in the timescale of the phase transition. From the current data it is not possible to determine whether it is only the size that accounts for the difference between the homogeneous and heterogeneous phase transition times, or if the presence of CO$_2$ leads to an additional inhibition.

The transition from phase II to phase III in the presence of a second substance in the aerosol phase is faster in a bath gas of $N_2$ than He, as was previously observed for the homo-
geneous transition discussed in Section 5.3.3. For a similar concentration of \( n{-}C_4H_{10} \) in the cooling cell, and with a ratio of \( n{-}C_4H_{10}:CO_2 \) of 4:1, it takes around 90 minutes for half of the \( n{-}C_4H_{10} \) aerosols to convert to phase III in a bath gas of \( N_2 \), but it is estimated to take around 400 minutes in a bath gas of \( He \). As in the case of the transition in the absence of a second substance, this effect can probably be explained by considering the size of the aerosols in the two bath gases. Fig. 5.11 shows the evolution of the mean particle radius over the measurement timescale in the presence of \( CO_2 \) in the aerosol phase. The particles were assumed to be composed of pure \( n{-}C_4H_{10} \) for the purposes of the size determination. It can be seen that, as in the homogeneous case, particle growth is more efficient in \( N_2 \) than in \( He \), and hence the phase transition time is shorter.

## 5.4 Summary

\( C_4H_{10} \) could be involved in cloud processes on Titan, possibly contributing to the coating of haze particles.\(^{108}\) It is therefore important to understand the possible phases of \( C_4H_{10} \) which could exist in the aerosol phase under conditions relevant for Titan, and the dynamics of transitions between these phases. An understanding of the spectroscopic signatures of these phases might also be important for confirming or excluding the presence of these condensates in the atmosphere of Titan.

The phase behavior of unsupported aerosol particles of \( n{-}C_4H_{10} \) under conditions relevant for the lower atmosphere of Titan has been studied using rapid scan FTIR spectroscopy. Two phase transitions and hence three phases of \( n{-}C_4H_{10} \) aerosol particles were observed. In contrast to aerosols of \( C_3H_8 \),\(^ {223} \) \( n{-}C_4H_{10} \) particles readily crystallize under these conditions. The first transition observed was from an amorphous-annealed phase to the metastable crystalline phase II, while the second transition was from phase II to the stable crystalline phase III. For the first transition the pure volume and surface nucleation constants were found to be
\[
J_V = 10^{12} - 10^{14} \text{ cm}^{-3} \text{ s}^{-1} \quad \text{and} \quad J_S = 10^{13} - 10^{15} \text{ cm}^{-2} \text{ s}^{-1},
\]
and for the second transition
\[
J_V = 10^9 - 10^{11} \text{ cm}^{-3} \text{ s}^{-1} \quad \text{and} \quad J_S = 10^{11} - 10^{13} \text{ cm}^{-2} \text{ s}^{-1}.
\]
These studies of \( n{-}C_4H_{10} \) aerosols show that solid condensates would dominate in the lower atmosphere of Titan. At equilibrium \( n{-}C_4H_{10} \) condensates would be likely to exist in the crystalline phase III at 78 K. However,
the transition from phase II to phase III is relatively slow, and hence \( n-C_4H_{10} \) aerosols in the crystalline phase II could also impact cloud processes on Titan, depending on the particle formation conditions. These studies suggest that incorporation of \( N_2 \), the major atmospheric gas on Titan, is not significant for solid \( n-C_4H_{10} \) condensates. This is contrast to \( n-C_5H_{12} \) aerosols, for which some evidence of \( N_2 \) incorporation was suggested in similar studies.\(^{223}\)

It is possible that condensation of \( n-C_4H_{10} \) would occur in conjunction with that of other substances in the atmosphere of Titan.\(^{33}\) In these studies the phase behavior was therefore also considered for mixed aerosol systems of \( n-C_4H_{10} \) with \( C_2H_2 \), \( CO_2 \) or \( H_2O \). For the first transition of \( n-C_4H_{10} \) particles similar trends were observed as in the case of \( C_2H_6 \) and \( n-C_5H_{12} \) aerosols:\(^{223}\) crystallization was significantly accelerated in the presence of heterogeneous ice nuclei. For the second transition from phase II to phase III the presence of another substance seems to influence the phase transition through modifying the particle size distribution and possibly by inhibiting the transition itself.

The aerosol studies were complemented by IR studies of thin films of pure \( n-C_4H_{10} \). The collected spectra, which include the first reported spectrum of liquid \( n-C_4H_{10} \) close to the melting point, helped to identify the phases in which the \( n-C_4H_{10} \) aerosols were found, and are expected to be of use for identifying phases of \( n-C_4H_{10} \) condensates in remote sensing studies. It should be noted that the band at \( \sim 1460 \text{ cm}^{-1} \) which was used to determine the phase of the \( n-C_4H_{10} \) aerosols here is not likely to be of use for distinguishing between various phases \( n-C_4H_{10} \) aerosols in the atmosphere of Titan owing to strong absorption bands of \( CH_4 \) and other hydrocarbons in this spectral region\(^{188}\) and a low signal-to-noise ratio.\(^{33,187}\) The region around 750 cm\(^{-1}\) is suitable for observations in the atmosphere of Titan,\(^{186}\) and as the spectrum of \( n-C_4H_{10} \) is sensitive to phase in this frequency range this region may be of particular interest for determining the phase of atmospheric \( n-C_4H_{10} \) condensates.
Table 5.1: Observed vibrational band positions in cm\(^{-1}\) for thin films of \(n\)-C\(_4\)H\(_{10}\) in various phases between 20 and 137 K.

<table>
<thead>
<tr>
<th>20 K amorphous</th>
<th>45 K amorphous-annealed</th>
<th>67 K phase</th>
<th>85 K phase III</th>
<th>83 K phase II</th>
<th>110 K phase I</th>
<th>137 K liquid</th>
<th>Conformer(^{[a]}) assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1469.5 (+)</td>
<td>1468.9</td>
<td>1472.5</td>
<td>1472 (sh)</td>
<td>1470.2</td>
<td>1469.2</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1462.9</td>
<td>1461.0</td>
<td>1466.2</td>
<td>1464.7</td>
<td>1463.1</td>
<td>1459.6</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1450 (sh)</td>
<td>1449 (sh)</td>
<td>1449.7</td>
<td>1446.4</td>
<td>1449.6</td>
<td>1450.0 (sh)</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1435 (sh)</td>
<td>1436 (sh)</td>
<td>1433.9 (vw)</td>
<td>1436.0 (w)</td>
<td>1391.4 (vw)</td>
<td>1393.9 (sh)</td>
<td>T, G(^{#})</td>
<td></td>
</tr>
<tr>
<td>1391.0</td>
<td>1392.0</td>
<td>1390.9</td>
<td>1380.2</td>
<td>1380.9 (vw)</td>
<td>1376.2</td>
<td>T, G(^{#})</td>
<td></td>
</tr>
<tr>
<td>1377.6</td>
<td>1377.2</td>
<td>1376.2</td>
<td>1367.7</td>
<td>1366.8</td>
<td>1363.6</td>
<td>T, G(^{#})</td>
<td></td>
</tr>
<tr>
<td>1361.1</td>
<td>1360.3</td>
<td>1359.8</td>
<td>1291.1</td>
<td>1290.8</td>
<td>1290.3</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1343.5 (-)</td>
<td>1300.6</td>
<td>1301.7 (w)</td>
<td>1289.5</td>
<td>1289.3</td>
<td>1287.4</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1108.7 (w)</td>
<td>1180.7 (w)</td>
<td>1183.5 (vw)</td>
<td>1284.6 (sh)</td>
<td>1284.1 (vw)</td>
<td>1285.0 (vw)</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1168.7 (vw)(-)</td>
<td>1150.0 (vw)</td>
<td>1150.1 (vw)</td>
<td>1257.0 (w)</td>
<td>1256.8 (vw)</td>
<td>1256.2 (w)</td>
<td>T, G(^{#})</td>
<td></td>
</tr>
<tr>
<td>1132.4 (-)</td>
<td>1132.6 (w)</td>
<td>1132.5</td>
<td>1180.2</td>
<td>1180.2</td>
<td>1150.3 (w)</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>1076.1 (vw)(-)</td>
<td>1057.4 (vw)</td>
<td>1075.9</td>
<td>1132.5</td>
<td>1132.5</td>
<td>1132.5</td>
<td>G(^{#})</td>
<td></td>
</tr>
<tr>
<td>1009.7 (vw)</td>
<td>1009.7 (vw)</td>
<td>1009.7 (vw)</td>
<td>1009.7 (vw)</td>
<td>1009.7 (vw)</td>
<td>1009.7 (vw)</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>990 (vw)</td>
<td>991.0 (vw)</td>
<td>994 (vw)</td>
<td>994.6 (w)</td>
<td>994.6 (w)</td>
<td>994.6 (w)</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>978.7 (-)</td>
<td>964.2 (+)</td>
<td>963.8</td>
<td>963.1</td>
<td>963.1</td>
<td>964.7</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>954.7 (-)</td>
<td>947.1 (+)</td>
<td>946.7</td>
<td>948.9 (sh)</td>
<td>948.9 (sh)</td>
<td>947.4</td>
<td>T, G(^{#})</td>
<td></td>
</tr>
<tr>
<td>836.6 (vw)</td>
<td>836.6 (vw)</td>
<td>836.6</td>
<td>945.4</td>
<td>945.4</td>
<td>945.4</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>804.0 (w)</td>
<td>804.8 (w)</td>
<td>803.0</td>
<td>942.3</td>
<td>942.3</td>
<td>942.3</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>788.8 (-)</td>
<td>790 (vw)</td>
<td>790 (vw)</td>
<td>731.6</td>
<td>731.6</td>
<td>731.6</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>746.7 (-)</td>
<td>747.3</td>
<td>747.3</td>
<td>732.2</td>
<td>732.2</td>
<td>732.2</td>
<td>T(^{#})</td>
<td></td>
</tr>
<tr>
<td>730.5 (+)</td>
<td>729.8</td>
<td>729.8</td>
<td>730.8</td>
<td>730.8</td>
<td>730.8</td>
<td>T(^{#})</td>
<td></td>
</tr>
</tbody>
</table>

\(^{-}\)(+): decrease/increase in intensity upon annealing, (vw): very weak, (w): weak, (sh): shoulder, T: trans conformer, G: gauche conformer, \(^{[a]}\)conformational assignments based on \(^{[216]}\)Snyder and \(^{[230]}\)Harada et al.

110
Chapter 6

Infrared Extinction Spectra of Aerosols with Relevance to Planetary and Lunar Atmospheres.

Note: This chapter was published in the Journal of Astronomical Data in 2012 with the goal to provide IR spectra of single component aerosols relevant to planetary and lunar atmospheres studied by Signorell and co-workers since 2006. This includes all hydrocarbon aerosols studied in this thesis (ethane (C₂H₆), propane (C₃H₈), normal-butane (n-C₄H₁₀), normal-pentane (n-C₅H₁₂)) and aerosols studied by other group members (methane (CH₄), ethylene (C₂H₄), acetylene (C₂H₂), carbon dioxide (CO₂), ammonia (NH₃), sulfur dioxide (SO₂)).

Part of the publication is to provide data that readers can access through the journal’s website (www.vub.ac.be/STER/JAD/jad.htm). The data described as machine readable data in this chapter therefore refers to the data accessible through the website and no spectra are shown in form of figures here, except for CH₄.

6.1 Introduction

Chapter 3 to Chapter 5 discussed the phase behavior of aerosol particles of the C₂-C₅ n-alkanes at 78 K and their potential role for cloud formation in Titan’s atmosphere. Aerosol and clouds are not only a feature of Titan, but also of a wide range of planetary and lunar atmospheres, for example those of Mars, Jupiter, Saturn, Uranus and Neptune.
There remains considerable uncertainty surrounding the physical and optical properties of aerosol particles and cloud condensates.\textsuperscript{29,236–238} This uncertainty leads to difficulty in determining the abundances, distributions and roles of aerosols and clouds in the relevant climate systems. The uncertainty can also greatly complicate, and limit the accuracy of the retrieval of information from remote sensing data and atmospheric modeling studies.\textsuperscript{239,240}

While measurements on thin films and bulk samples can be used to determine the characteristic spectral fingerprint of a given substance, such measurements cannot account for the effects of particle properties, for example shape and morphology, on aerosol spectra. Through a combination of laboratory measurements and novel theoretical approaches, Signorell and co-workers have developed a thorough understanding of the molecular basis for the characteristic spectral signatures of aerosol particles in the mid infrared (mid-IR).\textsuperscript{6} Through this work it has been demonstrated that mid-IR spectra can be used to determine a range of the physical properties of aerosols, for example particle shape, morphology, phase and crystal structure.\textsuperscript{6,110,134,149–151,161,163,172,175,176,218,241–245} Briefly, the laboratory measurements involve the generation of aerosol ensembles in a custom-built cooling cell, the conditions within which can be tuned to represent a range of lunar and planetary atmospheres.\textsuperscript{163,175} Once generated, mid-IR absorption spectra of the particle ensembles are recorded in transmission using a Fourier transform spectrometer. The theoretical approaches used to rationalize the collected spectra include vibrational exciton calculations, density functional calculations, and molecular dynamics and Monte Carlo simulations.

As mid-IR spectra can be used to elucidate aerosol properties, it follows that such information can contribute to reducing the uncertainty surrounding aerosol physical and optical properties in astronomical studies, and also to account for the effect of aerosol extinction on planetary processes. Provided the factors affecting aerosol spectra are understood, such spectra can be used to detect and characterize aerosols in planetary atmospheres. Laboratory spectra are therefore collected here as machine-readable data for a range of aerosols relevant to planetary and lunar atmospheres such as those mentioned above, with the aim of providing a convenient source of reference data for astrophysical studies. Wherever relevant, spectra characteristic of several phases and crystal structures for each given substance are presented.
The spectra presented here are for single-component aerosol particles; spectra for mixed-composition particles will follow in a subsequent publication. In most cases a detailed analysis of the molecular basis of the characteristic spectral signatures is available in a previous publication, while in the case of a few substances this will be the subject of future contributions.

The substances for which aerosol spectra are presented in this chapter are listed in Table 6.1, along with the normal melting point (at 1 atmosphere) of the substance and examples of atmospheric environments in which such particles are thought or have been confirmed to be present. The data are provided for the spectral region from around 6000 to 500 cm\(^{-1}\), with the exact range presented varying slightly for each data set. This range includes the 4.6 to 5.8 \(\mu m\) window useful for observations of methane-rich atmospheres such as that of Titan.

### Table 6.1: Substances for which aerosol spectra are presented, with normal melting points of bulk substances and examples of atmospheres in which the aerosols are thought or have been confirmed to be present

<table>
<thead>
<tr>
<th>Aerosol substance</th>
<th>Melting point / K</th>
<th>Examples of relevant atmospheric environments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane CH(_4)</td>
<td>91</td>
<td>Neptune([a])–([e]) Uranus([a]),([f]),([g]) Titan([i]),([j]),([k])</td>
</tr>
<tr>
<td>Ethane C(_2)H(_6)</td>
<td>90</td>
<td>Titan([o])</td>
</tr>
<tr>
<td>Propane C(_3)H(_8)</td>
<td>85</td>
<td>Titan([o])</td>
</tr>
<tr>
<td>(\alpha)-Butane C(_4)H(_10)</td>
<td>135</td>
<td>Titan([o]),([n])</td>
</tr>
<tr>
<td>(\alpha)-Pentane C(_5)H(_12)</td>
<td>143</td>
<td>Titan([o])</td>
</tr>
<tr>
<td>Acetylene C(_2)H(_2)</td>
<td>192</td>
<td>(sublimation) Neptune and Uranus([i]) Titan([o])</td>
</tr>
<tr>
<td>Ethylene C(_2)H(_4)</td>
<td>104</td>
<td>Titan([o])</td>
</tr>
<tr>
<td>Ammonia NH(_3)</td>
<td>195</td>
<td>Jupiter and Saturn([m])</td>
</tr>
<tr>
<td>Carbon dioxide CO(_2)</td>
<td>195</td>
<td>(sublimation) Titan([o]) Mars([j])</td>
</tr>
<tr>
<td>Sulfur dioxide SO(_2)</td>
<td>201</td>
<td>Io and Europa([m])</td>
</tr>
</tbody>
</table>

\([a]\) Smith et al.\(^{224}\), \([b]\) Gibbard et al.\(^{225}\), \([c]\) Max et al.\(^{225}\), \([d]\) Sanchez-Lavega et al.\(^{226}\), \([e]\) Karkoschka and Tomasko\(^{227}\), \([f]\) Lindal et al.\(^{228}\), \([g]\) Karkoschka and Tomasko\(^{229}\), \([h]\) Tomasko et al.\(^{230}\), \([i]\) Fulchignoni et al.\(^{231}\), \([j]\) Hueso and Sanchez-Lavega\(^{232}\), \([k]\) Tokano et al.\(^{233}\), \([l]\) Atreya et al.\(^{234}\), \([m]\) Rannou et al.\(^{235}\), \([n]\) Griffith et al.\(^{236}\), \([o]\) Coustenis et al.\(^{237}\), \([p]\) Curtis et al.\(^{238}\), \([q]\) Lara et al.\(^{239}\), \([r]\) Navarro-Gonzalez et al.\(^{240}\), \([s]\) Courtin\(^{241}\), \([t]\) Montmessin et al.\(^{242}\), \([u]\) Sandford and Allamandola\(^{243}\), \([v]\) Nash and Betts\(^{244}\), \([w]\) Schriver-Mazzuoli et al.\(^{245}\), \([x]\) Spencer et al.\(^{246}\)

### 6.2 Experimental

A brief summary of the experimental set-up is provided here; detailed descriptions can be found in Chapter 2 and elsewhere.\(^{163,175}\) Ensembles of single-component aerosols were generated by injecting a warm (temperature = 292 K) gas-phase sample of the aerosol substance of interest into a cold bath gas present in a custom-built cooling cell (temperature of the bath
gas: 4-95 K). Supersaturation of the sample gas in the cell leads to particle formation. In these measurements the particles typically vary in size from a few tens to several hundreds of nanometers in diameter; in general the particle size increases with time after formation. The particle number concentration in the cell is typically $10^4$ to $10^9$ cm$^{-3}$. The temperature, pressure and gas-phase composition in the cooling cell can be controlled, and hence it is possible to simulate the conditions present in a wide range of planetary and lunar atmospheres. Liquid helium or nitrogen is used as a coolant, and heaters are employed to access temperatures above the coolant boiling point.

Mid-IR absorption spectra of the aerosol ensembles were recorded in transmission in the region from approximately 6000 to 500 cm$^{-1}$ using a rapid-scan FTIR spectrometer (Bruker IFS 66v/S). The spectral resolutions used in these measurements were between 0.25 and 1 cm$^{-1}$.

In the spectra presented here the bath gas was either N$_2$ or He; in some cases aerosol phase changes are observed to proceed more rapidly in He than N$_2$, and hence the choice of the bath gas was determined by the dynamics of the relevant phase changes and the measurement timescale, with the objective of observing as many aerosol phases and/or crystal structures as possible. The aerosol substances were injected into the cell diluted by a factor of around $10^3$ in the major bath gas present in the cell.

### 6.3 Spectra of Pure Aerosols

Table 6.2 lists the aerosol spectral data files which accompany this manuscript as machine readable data, along with the dominant aerosol phase or crystal structure sampled, the time after injection of gases at which the spectrum was recorded, the bath gas used, the temperature at which the spectrum was recorded and the spectral range presented. As the spectra are collected for an aerosol ensemble, it is often the case that the spectrum represents a sum of contributions from two or more phases. The spectra have been provided in their original form, without any attempt to separate out the contributions from each phase, as such a task would require assumptions about the abundance and size distribution of particles in each phase. Each spectral data set has been normalized relative to the largest peak present in the spectrum arising from the substance of interest (i.e. neglecting impurities).
For measurements performed in a bath gas of N$_2$ at temperatures close to the boiling point of N$_2$, it is observed that N$_2$ is incorporated into liquid aerosol particles, but is excluded as they crystallize.\cite{183,184,197} The consequences of this phenomenon for the aerosol spectra are discussed in Section 6.4. It is not expected that He is incorporated into the particles for measurements carried out at temperatures of around 78 K. In certain cases weak signals are observed around 3200 cm$^{-1}$ and 2360 cm$^{-1}$. These signals arise from trace water and CO$_2$, respectively, and are the result of small amounts of ambient air entering the optical path or the gas samples during their preparation, or, in the case of the signal at 3200 cm$^{-1}$, from the occurrence of water-ice on the window of the cooled detector.

The presented spectra were recorded at varying times after the injection of gas into the cell, depending upon the aerosol phase of interest. As well as often changing phase, the particles also tend to increase in size with increasing time after formation, which gives rise to the increasingly-slanted baselines observed in the recorded spectra, a result of elastic scattering of light by large particles.\cite{4} The presented spectra have not been corrected for such scattering signatures. Owing to the contribution of scattering to light attenuation by particles, the presented data are extinction, rather than absorption, spectra. Extinction is the attenuation of light by absorption and scattering by particles and is defined, in the same way as absorbance, as $\log_{10}(I_0/I)$, where $I_0$ is the light incident on the sample and $I$ is the light transmitted through the sample.

In most cases the spectral data have been discussed in detail in previous publications (as indicated in Table 6.2), or will be the subject of future publications (in the case n-C$_4$H$_{10}$). Therefore only a brief summary of pertinent experimental or analytical details are provided here for each of the aerosol substances presented. A graphical representation of the aerosol spectra has been provided as in the case of CH$_4$ aerosols (Figs. 6.1 and 6.2) for illustrative purposes. Where precise band positions are provided they refer to the position of maximum peak intensity.

6.3.1 Methane

The mid-IR extinction spectra of solid CH$_4$ aerosols in three phases were measured by Signorell and Jetzki in 2007.\cite{110} The average particle radius was 5 nm, and the particle number concen-
Figure 6.1: IR extinction spectra of solid CH\textsubscript{4} aerosols for particles consisting of (A) amorphous CH\textsubscript{4}, \( T < 91 \) K, (B) phase I CH\textsubscript{4}, 20.4 K < \( T < 91 \) K, and (C) a core of phase II CH\textsubscript{4} with phase I CH\textsubscript{4} present at the surface, \( T = 8 \) K. The slanted baseline in this spectrum arises from light scattering by large particles.

Concentration \( \sim 10^9 \) cm\textsuperscript{-3}. The particles were generated in a bath gas of He. The normalized spectra are provided from 6000 to 1000 cm\textsuperscript{-1} and are presented graphically in Fig. 6.1. The two IR absorption bands observed arise from excitation of the triply degenerate stretching mode \( \nu_3 \) at \( \sim 3010 \) cm\textsuperscript{-1} and the triply degenerate bending mode \( \nu_4 \) at \( \sim 1300 \) cm\textsuperscript{-1}. The three spectra shown in Fig. 6.1 are for particles consisting of (A) amorphous CH\textsubscript{4}, temperature \( (T) < 91 \) K (ch4\textsubscript{1}), (B) phase I CH\textsubscript{4}, 20.4 K < \( T < 91 \) K (ch4\textsubscript{2}), and (C) a core of phase II CH\textsubscript{4} with phase I CH\textsubscript{4} present at the surface, \( T = 8 \) K (ch4\textsubscript{3}).

Fig. 6.2 shows the \( \nu_3 \) and \( \nu_4 \) bands in more detail. The shapes of the bands are characteristic of particles in a given phase, as has been determined by comparison with theory.\textsuperscript{110} For example, the unstructured, slightly asymmetric bands shown in part A are characteristic of particles consisting of amorphous CH\textsubscript{4}, the symmetric bands in part B are characteristic of particles consisting of phase I CH\textsubscript{4}, and the structured peaks with shoulders in part C are characteristic of particles consisting of a combination of phase I and phase II CH\textsubscript{4}. The slanted baseline in this spectrum arises from light scattering from large particles;\textsuperscript{3} this effect can be observed in many of the spectra presented here, often to a greater extent, which indicates that even larger particles are present.
Figure 6.2: IR extinction bands ($\nu_3$ at $\sim 3010$ cm$^{-1}$ and $\nu_4$ at $\sim 1300$ cm$^{-1}$) of solid CH$_4$ aerosols for particles consisting of (A) amorphous CH$_4$, $T < 91$ K, (B) phase I CH$_4$, 20.4 K $< T < 91$ K, and (C) a core of phase II CH$_4$ with phase I CH$_4$ present at the surface, $T = 8$ K.

6.3.2 Ethane

The particle phase dependence of the mid-IR extinction spectrum of C$_2$H$_6$ aerosols has been discussed in detail in Chapter 3$^{111,183,197}$. Briefly, upon injection of C$_2$H$_6$ gas into the cell, which is held at 78 K, supercooled liquid C$_2$H$_6$ droplets are formed which freeze over time. The spectra provided were recorded with increasing time after injection of C$_2$H$_6$ into the cell, and hence chart the progressive freezing of the C$_2$H$_6$ particles. The spectra c2h6_1, c2h6_2 and c2h6_3 correspond to supercooled liquid particles, combined phase I and phase II particles, and phase II particles, respectively. It has not been attempted to separate the contributions from the different phases in spectrum c2h6_2; difference spectra representative of phase I and II C$_2$H$_6$ aerosols have however been provided elsewhere.$^{197}$

In particular the $\nu_8$, $\nu_6$ and $\nu_9$ C$_2$H$_6$ bands, at 1463, 1370, and 819 cm$^{-1}$, respectively, are sensitive to the particle phase; of these the narrow features of the $\nu_9$ band for solid C$_2$H$_6$ make this band particularly useful for distinguishing between spectra arising from liquid and solid particles. c2h6_1 to c2h6_3 were recorded using a relatively high concentration of C$_2$H$_6$ in the cooling cell. The relatively weak absorption bands around 1600 to 600 cm$^{-1}$ are highly sensitive to phase, and using a high concentration of C$_2$H$_6$ allows the features of these bands to be examined in detail. The relatively strong absorption band at around 3000 cm$^{-1}$ is however saturated at this concentration of C$_2$H$_6$, and hence these spectra are only provided from 2800
to 600 cm\(^{-1}\). The band at around 3000 cm\(^{-1}\) is insensitive to particle phase; a spectrum for supercooled liquid C\(_2\)H\(_6\) particles is provided as c2h6.4, recorded with a lower concentration of C\(_2\)H\(_6\) in the cell at which this band is not saturated. In spectrum c2h6.4, the broad weak signal observed around 3200 cm\(^{-1}\) arises from trace water which resulted from small amounts of water contaminating the gas sample during its preparation, or possibly from the occurrence of water-ice on the window of the cooled detector. Finally, c2h6.5 is the same spectrum as c2h6.1, however provided for a wider spectral range of 6000 to 600 cm\(^{-1}\). Although the band at around 3000 cm\(^{-1}\) is saturated in this spectrum, owing to the high concentration of C\(_2\)H\(_6\) in the cell, several relatively weak C\(_2\)H\(_6\) bands in the region from 4500 to 3200 cm\(^{-1}\) can be observed under these conditions. This region is useful for ground-based observations as it overlaps with the spectral window in the atmosphere of Earth centered at around 2.2 \(\mu\)m.\(^{256}\)

### 6.3.3 Propane

C\(_3\)H\(_8\) has certain properties which are unusual among the alkanes: it has an anomalously low melting point,\(^{191,192}\) and it has been observed that an anomalously high degree of supercooling is possible in bulk samples before crystallization occurs.\(^{145,193,198}\) The spectra of liquid C\(_3\)H\(_8\) particles (measured above the melting point, at \(\sim 95\) K), and of C\(_3\)H\(_8\) particles below the melting point are presented here, as c3h8.1 and c3h8.2, respectively. It should be noted that the fluctuations in the baseline of the warm spectrum (c3h8.1) result from temperature instabilities of the sample and optics which arise as a result of introducing a heat source to the experimental chamber. In these spectra, the broad weak signal observed around 3200 cm\(^{-1}\) again arises from trace water contaminating the gas sample, or possibly from the occurrence of water-ice on the window of the cooled detector.

It can be seen that the bands in this pair of spectra match very closely, and further, a double-peaked feature at 1460 cm\(^{-1}\) which has previously been observed in measurements on thin films of crystalline C\(_3\)H\(_8\) is not present in the aerosol spectrum.\(^{33}\) It is therefore reasoned that the spectrum c3h8.2 arises from either supercooled liquid, highly viscous, or amorphous, rather than crystalline C\(_3\)H\(_8\) particles. Indeed, despite considerable efforts, and under a range of conditions, crystallization of C\(_3\)H\(_8\) particles has not been observed in these measurements.
The anomalously slow crystallization of C$_3$H$_8$ aerosols was discussed in detail in Lang et al.\textsuperscript{223}\textsuperscript{1}

### 6.3.4 $n$-Butane

$n$-C$_4$H$_{10}$ has a melting point of 135 K, and hence it is likely that the aerosol particles condense directly to the solid state upon introduction of $n$-C$_4$H$_{10}$ gas to the cell when at 78 K. That the particles are solid immediately after injection of gas to the cell is supported by the observation that the bands in the earliest spectrum after gas injection, c4h10\_1, match closely with those reported by Axford and Rank for solid $n$-C$_4$H$_{10}$ at $\sim$ 7 K; in particular the bands at 1233 and 1133 cm$^{-1}$ which are characteristic of liquid $n$-C$_4$H$_{10}$ are missing.\textsuperscript{224} Three phases of $n$-C$_4$H$_{10}$ aerosols were observed in these measurements. Spectra are provided for each of the three phases observed, following the assignment of Cangeloni and Schettino: the observed absorption bands present in the spectra c4h10\_1, c4h10\_2 and c4h10\_3 match closely with those in the spectra attributed by Cangeloni and Schettino to a solid disordered phase ("phase I", 108 K),\textsuperscript{136} a metastable monoclinic phase ("phase II", 77 K), and a triclinic phase ("phase III", 77 K), respectively,\textsuperscript{136} although it should be noted that in c4h10\_2 weak features of phase I are still present. The crystal structure assignments by Cangeloni and Schettino were purely based on the band shape and splitting observed in IR and Raman spectra.\textsuperscript{136} Neutron powder diffraction experiments performed by Refson and Pawley finally found all solids to be monoclinic.\textsuperscript{225} Detailed spectral assignments and analysis of the kinetics of the phase transitions of C$_4$H$_{10}$ aerosols were described in Chapter 5 and will be the subject of a forthcoming publication.\textsuperscript{200} In these spectra, the broad signals observed around 3200 cm$^{-1}$ and 2360 cm$^{-1}$ arise from trace ambient air entering the optical path, and potentially from trace water contamination in the gas sample.

### 6.3.5 $n$-Pentane

Similarly to $n$-C$_4$H$_{10}$, $n$-C$_5$H$_{12}$ has a high melting point (143 K), and hence it is likely that the aerosol particles condense directly to the solid state upon introduction of $n$-C$_5$H$_{12}$ gas to the cell when at 78 K. That the particles are solid immediately after injection of gas to the

\textsuperscript{1}See Chapter 4.3.1 for discussion of aerosol particles and Chapter 7.3.2 for thin film measurements of C$_3$H$_8$ confirming that the observed aerosol particles at 78 K are indeed liquid.

\textsuperscript{ii}The spectrum c4h10\_1 was identified as "amorphous-annealed" with the help of thin film measurements as discussed in Chapter 5.
cell is again supported by the observation that the bands in the earliest spectrum after gas injection, c5h12.1, match closely with those reported for solid $n$-C$_5$H$_{12}$ at $\sim$ 78 K by Axford and Rank.$^{211}$ For example, the bands at 1342 and 907 cm$^{-1}$ which are characteristic of liquid $n$-C$_5$H$_{12}$ are missing. A single phase transition is observed under these conditions, reasoned to be that from a disordered solid state (likely amorphous solid rather than supercooled liquid, as discussed above) (c5h12.1) to a crystalline phase (c5h12.2). The bands around 1460 and 1380 cm$^{-1}$ are particularly useful for distinguishing between spectra arising from particles in differing phases. The spectral features of C$_5$H$_{12}$ aerosols and the kinetics of this phase transition are discussed in Lang et al. (Chapter 4.3.2).$^{223}$ In these spectra a broad signal is observed around 3200 cm$^{-1}$, arising from trace water contaminating the gas sample, or from the occurrence of water-ice on the window of the cooled detector.

If a higher concentration of $n$-C$_5$H$_{12}$ is present in the cell, soon after particle formation (c5h12.3), spectral features consistent with the presence of at least two conformational isomers of $n$-C$_5$H$_{12}$ are observed. As the observed phase transition proceeds, several of these spectral features are lost (c5h12.4), reasoned to be those associated with less stable rotamers. Several of the bands which are lost, for example the bands at 1238 and 908 cm$^{-1}$, coincide with those attributed to less stable rotamers of liquid $n$-C$_5$H$_{12}$ in vibrational studies$^{214,216}$ and calculations.$^{257}$ These observations would be consistent with initial fixing of unstable rotamers during rapid freezing to an amorphous state, followed by conversion to the stable anti rotamers, as has previously been observed in work using matrix-isolated alkanes by Goodman et al.$^{196}$ This process and the relevant spectral assignments were discussed in detail in Lang et al.$^{223}$

### 6.3.6 Ethylene / Ethene

The particle phase dependence of the mid-IR extinction spectrum of C$_2$H$_4$ aerosols has been discussed in detail in Wang et al.$^{134}$ Briefly, upon injection of C$_2$H$_4$ into the cell, which contains 900 mbar He held at 78 K, supercooled liquid C$_2$H$_4$ droplets are formed which freeze over time. The normalized spectra provided from 5000 to 600 cm$^{-1}$ as c2h4.1, c2h4.2 and c2h4.3 were recorded at increasing times after injection of C$_2$H$_4$ into the cell, and hence represent

---

$^{iii}$The phase behavior of $n$-C$_5$H$_{12}$ aerosol particles has been discussed in detail in Chapter 4.3.2. The initial phase formed in N$_2$ as bath gas was identified as “amorphous-annealed” via IR spectroscopy of a vapor-deposited film of $n$-C$_5$H$_{12}$ which is discussed in detail in Chapter 7.3.3.
the progressive freezing of C\textsubscript{2}H\textsubscript{4} particles. The spectra c2h4\textsubscript{1}, c2h4\textsubscript{2} and c2h4\textsubscript{3} correspond to supercooled liquid particles, combined metastable “a-structure” and stable P2\textsubscript{1}/n “b-structure” particles, and particles composed almost entirely of C\textsubscript{2}H\textsubscript{4} in the P2\textsubscript{1}/n “b-structure”, respectively. The band arising from excitation of the CH\textsubscript{2}-scissor vibration $\nu_{12}$ at $\sim 1440$ cm$^{-1}$ is particularly useful for determining the phase of C\textsubscript{2}H\textsubscript{4} particles. It should be noted that signatures of gas phase C\textsubscript{2}H\textsubscript{4} can be seen in these spectra, and that these affect the appearance of the aerosol bands, particularly in the region around 950 cm$^{-1}$.

6.3.7 Acetylene / Ethyne

The mid-IR absorption spectra of solid C\textsubscript{2}H\textsubscript{2} aerosols in two crystal structures for temperatures between 78 K and 110 K were reported and rationalized by Preston et al.\textsuperscript{161} In this work the particle diameters were between $\sim 50$ and 500 nm, and the particle number concentrations between $10^4$ and $10^6$ cm$^{-3}$.

The two spectra presented as c2h2\textsubscript{1} and c2h2\textsubscript{2} are for particles consisting of polycrystalline C\textsubscript{2}H\textsubscript{2} and orthorhombic crystalline C\textsubscript{2}H\textsubscript{2} (produced by annealing polycrystalline particles by condensing C\textsubscript{2}H\textsubscript{6} onto them), respectively. The spectra are consistent with particles in a globular shape. The two strong IR absorption bands attributable to C\textsubscript{2}H\textsubscript{2} arise from excitation of the antisymmetric CH-stretching vibration $\nu_3$, at $\sim 3230$ cm$^{-1}$, and the bending vibration $\nu_5$, at $\sim 770$ cm$^{-1}$, while the weaker band at $\sim 1390$ cm$^{-1}$ is assigned to the $\nu_4 + \nu_5$ combination band.\textsuperscript{258} In the crystalline state the $\nu_5$ band is strongly influenced by the particle shape.\textsuperscript{161} The additional features apparent in spectrum c2h2\textsubscript{2} arise from C\textsubscript{2}H\textsubscript{6}, which is used to anneal the polycrystalline particles to a crystalline structure.

6.3.8 Carbon Dioxide

The mid-IR extinction spectra of solid CO\textsubscript{2} aerosols (cubic crystal structure) have been reported and rationalized by Signorell and co-workers.\textsuperscript{6,134,151,172,176,229} The absorption bands of CO\textsubscript{2} depend strongly on particle size, shape and morphology. Here the spectra of solid CO\textsubscript{2} aerosols with two particle shapes are presented. The aerosols were generated in a bath gas of N\textsubscript{2}. The spectra, normalized to the intensity of the band at $\sim 2360$ cm$^{-1}$, are provided from 4500 to 500 cm$^{-1}$. The spectra, co2\textsubscript{1} and co2\textsubscript{2}, are characteristic of crystalline particles in
the shape of truncated cubes\textsuperscript{229} and with an elongated particle geometry, respectively, as has been previously determined by modeling.\textsuperscript{176} It has been observed that a higher pressure in the cell favors the formation of cube-like particles, while a lower pressure favors an elongated particle geometry.\textsuperscript{176,259}

The two IR absorption bands observed arise from excitation of the antisymmetric stretching mode \( \nu_3 \), at \( \sim 2360 \text{ cm}^{-1} \) and the bending mode \( \nu_2 \), at \( \sim 770 \text{ cm}^{-1} \). The band at \( 2283 \text{ cm}^{-1} \) arises from \( ^{13}\text{CO}_2 \); it is not sensitive to particle shape as a result of the low abundance of \( ^{13}\text{C} \) (1.1\%).\textsuperscript{176} Weak bands at \( \sim 3600 \) and \( \sim 3700 \text{ cm}^{-1} \) arise from excitation of the combination vibrations \( 2
u_2 + \nu_3 \) and \( 2\nu_1 + \nu_3 \), respectively.

\subsection{6.3.9 Ammonia}

The effects of particle shape, surface phenomena and particle size on the mid-IR absorption spectra of solid \( \text{NH}_3 \) aerosols have been previously reported by Signorell and co-workers.\textsuperscript{243,245} Here spectra of solid crystalline \( \text{NH}_3 \) aerosols which were generated in a bath gas of He are presented. The spectra nh3\textsubscript{1} and nh3\textsubscript{2} were recorded at varying times after particle formation. As is the case for \( \text{CO}_2 \) aerosols, over time the particles become more elongated in shape. The spectra therefore correspond to varying mixtures of particles with a globular or elongated shape: the features of nh3\textsubscript{1} are dominated by globular shaped particles, while nh3\textsubscript{2} is dominated by particles with an elongated geometry. In the case of \( \text{NH}_3 \) aerosols only the \( \nu_2 \) band at \( 1067 \text{ cm}^{-1} \) is sensitive to particle shape.

Spectra nh3\textsubscript{1} and nh3\textsubscript{2} correspond to particles with diameters greater than \( \sim 10 \text{ nm} \), for which surface effects are negligible. For particles with sizes below 10 nm, however, surface effects (and hence particle size) play an important role in determining the spectral signatures. By varying the temperature in the cooling cell, it is possible to control the size of the particles which are formed. nh3\textsubscript{3}, nh3\textsubscript{4} and nh3\textsubscript{5} were recorded at cell temperatures of 80 K, 37 K and 21 K, respectively, and correspond to particles with a diameter of \( \sim 10 \text{ nm} \), 4 nm and 2 nm, respectively.\textsuperscript{248} Size-dependent features can be observed in the spectra both in the region of the \( \nu_2 \) band and the region around 3300 cm\textsuperscript{-1}.
6.3.10 Sulfur Dioxide

The mid-IR absorption spectra of solid SO$_2$ aerosols have been reported by Signorell and Jetzki. The average particle diameter was $\sim 50$ nm, and the particle number concentration $\sim 10^6$ cm$^{-3}$. The particles were generated in a bath gas of He. The spectra, normalized to the intensity of the band at 1335 cm$^{-1}$, are provided from 5000 to 600 cm$^{-1}$. Detailed modeling and experimental investigations demonstrated that the spectra, so$_2$.1 and so$_2$.2, are consistent with particles which are partially amorphous (observed for $60 < T < 90$ K) and amorphous (observed for $T < 10$ K), respectively. For these spectra the baseline has been corrected to compensate for the effect of carrying out measurements at varying temperatures.

The two IR absorption bands, observed at 1335 cm$^{-1}$ and 1149 cm$^{-1}$, arise from excitation of the antisymmetric stretching vibration $\nu_3$ and the symmetric stretching vibration $\nu_1$, respectively. Absorption bands of the isotopomer $^{34}$SO$_2$ appear to the low wavenumber side of these peaks.

6.4 Discussion

The uncertainties/stabilities in measured quantities are as follows:

1. Spectral resolution: 0.25 to 1 cm$^{-1}$.

2. Cell temperature: close to coolant boiling point (4 or 77 K) the temperature is stable to $\pm 1$ K; far from coolant boiling point the temperature is stable to $\pm 5$ K.

There are several general factors affecting the collected spectra:

1. For some spectra (i.e. C$_2$H$_6$, n-C$_5$H$_{12}$) recorded in a bath gas of N$_2$ at temperatures close to 77 K, it is likely that N$_2$ is incorporated into the particles, and that it is excluded during particle crystallization. Therefore for several of the liquid (or amorphous) spectra presented here it is important to note that bi-component particles are being sampled. By comparing spectra recorded in bath gases of N$_2$ and He, however, it has been determined that the incorporation of N$_2$ does not have a strong effect on the aerosol spectra.
2. These are ensemble measurements, and hence a distribution of particle sizes, shapes, phases and compositions contribute to the recorded spectra. In the sections above situations where more than one particle type contributes strongly to the observed spectra are highlighted.

3. The conditions under which the aerosols exist in planetary and lunar atmospheres can differ from those under which the spectra presented here were recorded. The most stable particle phase and the dynamics of aerosol phase changes are strongly dependent on temperature. The bath gas present (N₂ or He) has also been found to be important in determining the rate of aerosol phase changes. In general it has been found that the atmospheric pressure does not have a significant effect on aerosol phase dynamics within the range from 500 to 800 mbar, however it does have an effect on particle shape, for example in the cases of CO₂ and NH₃ aerosols.
Table 6.2: Summary of spectral data presented: ASCII filename, substance and relevant publication(s), dominant particle phase, time relative to injection (s), bath gas pressure (mbar), temperature at which recorded (K), spectral range (cm$^{-1}$)

<table>
<thead>
<tr>
<th>File.dat</th>
<th>Substance and references</th>
<th>Dominant particle phase</th>
<th>Time after injection</th>
<th>Bath gas, pressure</th>
<th>Temp. rec.</th>
<th>Spectral range</th>
</tr>
</thead>
<tbody>
<tr>
<td>ch4_1</td>
<td>Methane$^a$</td>
<td>Amorphous</td>
<td>0</td>
<td></td>
<td>&lt; 91</td>
<td></td>
</tr>
<tr>
<td>ch4_2</td>
<td></td>
<td>Crystalline phase I</td>
<td>~ 300</td>
<td>He, 400</td>
<td>20.4-91</td>
<td>6000-1000</td>
</tr>
<tr>
<td>ch4_3</td>
<td></td>
<td>Crystalline phase I and II</td>
<td>N/A$^1$</td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>c2h6_1</td>
<td></td>
<td>Liquid (supercooled)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c2h6_2</td>
<td>Ethane$^b$, $^c$</td>
<td>Liquid (supercooled)</td>
<td>531</td>
<td>N$_2$, 570</td>
<td>2800-600</td>
<td></td>
</tr>
<tr>
<td>c2h6_3</td>
<td></td>
<td>phase I and II solid</td>
<td>2540</td>
<td></td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>c2h6_4</td>
<td></td>
<td>Liquid (supercooled)</td>
<td>42</td>
<td>He, 800</td>
<td>6000-600</td>
<td></td>
</tr>
<tr>
<td>c2h6_5</td>
<td></td>
<td>Liquid (supercooled)</td>
<td>1</td>
<td>N$_2$</td>
<td>6000-600</td>
<td></td>
</tr>
<tr>
<td>c3h8_1</td>
<td>Propane$^d$</td>
<td>Liquid</td>
<td>1098</td>
<td>N$_2$, 800</td>
<td>95</td>
<td>5000-500</td>
</tr>
<tr>
<td>c3h8_2</td>
<td></td>
<td>Liquid (supercooled)</td>
<td>10</td>
<td>He, 800</td>
<td>78</td>
<td>5000-500</td>
</tr>
<tr>
<td>c3h10_1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c3h10_2</td>
<td>$n$-Butane$^e$</td>
<td>phase I solid</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c3h10_3</td>
<td></td>
<td>phase II solid</td>
<td>96</td>
<td>N$_2$, 800</td>
<td>78</td>
<td>6000-600</td>
</tr>
<tr>
<td>c5h12_1</td>
<td></td>
<td>phase II solid</td>
<td>5596</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c5h12_2</td>
<td>$n$-Pentane$^d$</td>
<td>Amorphous</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c5h12_3</td>
<td></td>
<td>Crystalline</td>
<td>2534</td>
<td>N$_2$, 800</td>
<td>78</td>
<td>6000-600</td>
</tr>
<tr>
<td>c5h12_4</td>
<td></td>
<td>Amorphous</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c2h2_1</td>
<td>Acetylene$^b$, $^f$</td>
<td>Polycrystalline</td>
<td>1</td>
<td>He, 500-900</td>
<td>79</td>
<td>5000-500</td>
</tr>
<tr>
<td>c2h2_2</td>
<td></td>
<td>Crystalline</td>
<td>N/A$^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c2h4_1</td>
<td>Ethylene$^c$</td>
<td>Liquid (supercooled)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c2h4_2</td>
<td></td>
<td>Combination of a and b structures (solid)</td>
<td>1</td>
<td>He, 900</td>
<td>79</td>
<td>5000-600</td>
</tr>
<tr>
<td>c2h4_3</td>
<td></td>
<td>b structure (P2$_1$/n, solid)</td>
<td>86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>co2_1</td>
<td>Carbon dioxide$^b$, $^c$, $^e$</td>
<td>Truncated cube shape crystalline</td>
<td>1</td>
<td>He, 950</td>
<td>78</td>
<td>4500-500</td>
</tr>
<tr>
<td>co2_2</td>
<td></td>
<td>Elongated shape crystalline</td>
<td>50</td>
<td>He, 900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nh3_1</td>
<td>Ammonia$^g$, $^m$</td>
<td>Globular shape crystalline</td>
<td>10</td>
<td>He, 50-1000</td>
<td>80</td>
<td>3600-800</td>
</tr>
<tr>
<td>nh3_2</td>
<td></td>
<td>Elongated shape crystalline</td>
<td>884</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nh3_3</td>
<td></td>
<td>10 nm crystalline</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nh3_4</td>
<td></td>
<td>4 nm crystalline</td>
<td>N/A</td>
<td>He, 50-1000</td>
<td>37</td>
<td>3500-800</td>
</tr>
<tr>
<td>nh3_5</td>
<td></td>
<td>2 nm crystalline</td>
<td>21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>so2_1</td>
<td>Sulfur dioxide$^n$</td>
<td>Partially amorphous</td>
<td>0</td>
<td>He, 10-1000</td>
<td>60</td>
<td>5000-600</td>
</tr>
<tr>
<td>so2_2</td>
<td></td>
<td>Amorphous</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Signorell and Jetzki$^{110}$, $^b$Wang et al.$^{133}$, $^c$Lang et al.$^{197}$, $^d$Lang et al.$^{223}$, $^e$Lang et al.$^{200}$, $^f$Preston et al.$^{151}$, $^g$Signorell$^{172}$, $^h$Signorell and Kunzmann$^{176}$, $^i$Jetzki et al.$^{243}$, $^j$Firanescu et al.$^{245}$, $^k$Signorell and Jetzki$^{150}$, Remarks: 1: after temperature change, 2: after annealing procedure.
Chapter 7

Infrared Spectra of Thin Films of the
n-Alkanes C$_2$-C$_5$

7.1 Introduction

Chapters 3 to 6 discussed the phase behavior of C$_2$-C$_5$ n-alkane aerosol particles at 78 K. The motivation was primarily the relevance to cloud properties in planetary and lunar atmospheres, especially Saturn’s moon Titan. However, several questions concerning the observed phases of the studied aerosol particles remained unresolved. For propane (C$_3$H$_8$) aerosol particles, for example, at 78 K no phase transition was observed on the timescale of the experiment. With support from literature it was concluded that C$_3$H$_8$ forms supercooled viscous liquid droplets. In the case of n-pentane (n-C$_5$H$_{12}$) we assumed that an amorphous solid formed upon particle formation in nitrogen (N$_2$) as bath gas since the survival of supercooled liquid droplets at 65 K below the melting point is rather unlikely.

The amount of literature available discussing mid-infrared (mid-IR) spectra of the solid phases of short-chained n-alkanes is limited. Therefore, thin films between 20 K and the respective melting points of all n-alkanes discussed in the previous chapters as aerosol particles were studied using infrared (IR) spectroscopy: ethane (C$_2$H$_6$), C$_3$H$_8$, n-butane (n-C$_4$H$_{10}$), and n-C$_5$H$_{12}$. The goal was to access as many solid phases as possible below the melting point of each substance, as well as to obtain a liquid IR spectrum just above it, and to then use the acquired spectra to confirm previous findings for observed aerosol phases, to identify the
observed phases in question (for C$_3$H$_8$ and n-C$_5$H$_{12}$ particles), and to compare our findings to literature data.

In this chapter the IR spectra of observed phases of thin films of C$_2$H$_6$, C$_3$H$_8$, and n-C$_5$H$_{12}$ between 20 K and the respective melting points are presented and compared to the aerosol spectra recorded at 78 K. Thin films of n-C$_4$H$_{10}$ and their use in identifying phases of n-C$_4$H$_{10}$ aerosol particles have been discussed in Chapter 5. The discussion will focus on the fingerprint region between 1550-700 cm$^{-1}$. The region of the CH-stretching mode between 3100-2750 cm$^{-1}$ will be included in the figures for completeness. However, this region is rather insensitive to phase changes and is therefore not further discussed.

Table 7.1 gives an overview of the known crystal structures and stable temperatures ranges for solid n-alkanes from C$_1$-C$_5$. In this thesis CH$_4$ in the solid was studied neither as aerosol particles nor as a thin film and is only included here for completeness.

### Table 7.1: Overview of solid n-alkanes from C$_1$-C$_5$ at pressures ≤ 1 bar

<table>
<thead>
<tr>
<th>Substance &amp; Phase</th>
<th>Stable Temperature Range (K)</th>
<th>Space Group</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ (T$_d$)</td>
<td>$20.4 &lt; T &lt; 90.69^{[a]}$</td>
<td>$Fm3m^{[d]}$</td>
<td>cubic$^{[a]}$</td>
</tr>
<tr>
<td>partially ordered, phase II</td>
<td>$T &lt; 20.4^{[a]}$</td>
<td>$Fm3c^{[a]}$</td>
<td>cubic$^{[a]}$</td>
</tr>
<tr>
<td>C$_2$H$<em>6$ (D$</em>{3d}$)</td>
<td>$89.83 &lt; T &lt; 90.35^{[c]}$</td>
<td>$I43m^{[a]}$</td>
<td>cubic$^{[a]}$</td>
</tr>
<tr>
<td>plastic crystalline, phase I</td>
<td>$89.73 &lt; T &lt; 89.83^{[c]}$</td>
<td>$P2_1/n^{[d]}$</td>
<td>monoclinic$^{[d]}$</td>
</tr>
<tr>
<td>metastable, phase III</td>
<td>$T &lt; 89.73^{[c]}$</td>
<td>$P2_1/n^{[d]}$</td>
<td>monoclinic$^{[d]}$</td>
</tr>
<tr>
<td>crystalline, phase II</td>
<td>$T &lt; 85.5^{[d]}$</td>
<td>$P2_1/c^{[h]}$</td>
<td>monoclinic$^{[h]}$</td>
</tr>
<tr>
<td>crystalline, phase $\beta$</td>
<td>$79.7 &lt; T &lt; 81.2^{[d]}$</td>
<td>$P2_1/c^{[h]}$</td>
<td>monoclinic$^{[h]}$</td>
</tr>
<tr>
<td>metastable, phase $\alpha$</td>
<td>$107.6 &lt; T &lt; 134.9^{[h]}$</td>
<td>$P2_1/c^{[d]}$</td>
<td>monoclinic$^{[d]}$</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$ (C$_{2v}$)</td>
<td>$T &lt; 107.6^{[b]}$</td>
<td>$P2_1/c^{[h]}$</td>
<td>monoclinic$^{[h]}$</td>
</tr>
<tr>
<td>R metastable crystalline, phase II</td>
<td>$T &lt; 143.4^{[b]}$</td>
<td>$Pbcn^{[e]}$</td>
<td>orthorhombic$^{[e]}$</td>
</tr>
</tbody>
</table>

*Symmetry of most stable molecular conformation, $^{[a]}$Signorell and Jetzki$^{[110]}$, $^{[b]}$Bini et al.$^{[26]}$, $^{[c]}$Pavese$^{[129]}$, $^{[d]}$Van Nes and Vos$^{[164]}$, $^{[e]}$Klimenko et al.$^{[144]}$, $^{[f]}$Pavese and Besley$^{[145]}$, $^{[g]}$Boese et al.$^{[192]}$, $^{[h]}$Refson and Pawley$^{[225]}$, $^{[i]}$Wei$^{[147]}$.
7.2 Experimental

The general experimental methods for thin film measurements are described in Chapter 2.2. A liquid and a vapor-deposited sample were prepared for each compound. The reason for two different sample preparations was that we wanted to access as many solid phases as possible and the number of occurring phases can be different for crystallization from a vapor-deposited solid or crystallization from the liquid phase.

All vapor-deposited samples were deposited at 20 K with a flow rate of 10 ccm onto a ZnSe substrate to obtain an initial amorphous solid. Subsequently, the sample was heated in increments of 2 K to temperatures of interest that were obtained from literature and was kept at each temperature for 2-5 minutes. Several IR spectra were recorded every 2-5 minutes at each temperature and only if two subsequent spectra did not show any change in the band shape, the temperature was further increased. A change in the band shape indicates a change in molecular conformation or the crystal structure, during which the sample was kept at a constant temperature and IR spectra were recorded every 5-10 minutes until no further change was observed.

To obtain a liquid sample of C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, or n-C\textsubscript{5}H\textsubscript{12}, the sample gas of interest was injected into an enclosed optical cell above its melting point. C\textsubscript{2}H\textsubscript{6} was injected at ∼120 K with a flow rate of 100 ccm, C\textsubscript{3}H\textsubscript{8} at ∼100 K with a flow rate of 500 ccm, and n-C\textsubscript{5}H\textsubscript{12} at ∼200 K with a flow rate of 100 ccm. In the case of n-C\textsubscript{5}H\textsubscript{12} the deposition took several minutes and only cooling of the sample finally led to enough condensation on the cell windows to obtain an acceptable IR spectrum of the liquid.

After an initial liquid spectrum was obtained the sample was cooled to the melting point and heated and cooled several times a few degrees above and below it with the goal to observe supercooling, crystallization and melting. The sample was then cooled to 78 K for comparison with the aerosol spectra obtained at 78 K. C\textsubscript{3}H\textsubscript{8} was further cooled to 65 K, 20 K below its freezing point, since according to literature C\textsubscript{3}H\textsubscript{8} is difficult to freeze and because at 78 K the IR spectrum indicated C\textsubscript{3}H\textsubscript{8} still to be liquid.\textsuperscript{193,198}

\textsuperscript{1}Temperatures of interest are, for example, previously observed transition temperatures such as observed in differential thermal analysis experiments by Takeda et al.\textsuperscript{210}
7.3 Results and Discussion

7.3.1 Ethane

7.3.1.1 Thin Film IR Spectra of Ethane

Fig. 7.1 presents the IR spectra of a thin film of C$_2$H$_6$ between 20-92 K in the regions of the CH-stretching mode between 3100-2750 cm$^{-1}$, the $\nu_8$ and $\nu_6$ bands between 1550-1320 cm$^{-1}$, and the $\nu_9$ band between 860-780 cm$^{-1}$. The band positions for all observed phases of the thin film of C$_2$H$_6$ between 20-92 K are summarized in Table 7.2.

a) Amorphous Ethane

Fig. 7.1A is the IR spectrum of C$_2$H$_6$ after vapor deposition at 20 K. The solid formed has an amorphous structure with broad and asymmetric bands found at 1461, 1368 (with a shoulder at 1365), and 816 cm$^{-1}$, and is in agreement with literature.$^{99}$

b) A metastable Phase of Ethane at 45 K

According to Wisnosky et al., deposition of C$_2$H$_6$ between 25-60 K leads to a mixture of two crystalline phases of C$_2$H$_6$, a mixture of phase II and a solid phase that was found to be metastable in respect of phase II.$^{262}$ Wisnosky et al. describes this metastable phase (from here on phase IV) to be ordered and crystalline and to be distinct from phase I and phase II of C$_2$H$_6$ and that it can be obtained in pure form by vapor deposition at $\sim$ 47 K. The spectrum of C$_2$H$_6$ deposited at 45 K is shown in Fig. 7.1B. The bands for the metastable phase IV were found at 1463, 1453, 1369, 1364, 821, and 815 cm$^{-1}$ which is in good agreement with the previous observation of phase IV by Wisnosky et al.$^{262}$ Comparing the metastable phase IV at 45 K to phase II at 24 K in Fig. 7.1C shows that the two phases are clearly different and that no contributions from phase II are found in the spectrum of phase IV, indicating that it must be in the pure form and that no mixture has formed.

One question that arises is if the deposit at 45 K, phase IV, could be one of the phases observed around 90 K, the melting point of C$_2$H$_6$. C$_2$H$_6$ has three solid phases close to the melting point that were first observed by Pavese$^{129}$ and Schutte et al.$^{130}$ using calorimetry
Figure 7.1: IR spectra collected from a thin film of C$_2$H$_6$ between 20 and 92 K. Spectra A to C were obtained by vapor deposition of C$_2$H$_6$ gas on a ZnSe substrate at 20 K followed by temperature increase. Spectra D and E were obtained by injection of C$_2$H$_6$ gas into an enclosed optical cell at 140 K and subsequent cooling. All spectra are baseline corrected.

Figure 7.2: IR spectrum of (A) C$_2$H$_6$ aerosol particles crystallized in phase II and (B) of supercooled liquid C$_2$H$_6$ after particle formation. Both spectra were obtained at 78 K. The CH-stretching region from 3050-2800 cm$^{-1}$ was obtained at a lower concentration than the fingerprint region between 1550-800 cm$^{-1}$. 
and nuclear-magnetic-resonance (NMR), respectively, as experimental methods.\footnote{Pavese found that the transition of the stable phase II into a metastable form (from here on phase III) can be observed upon heating at $T_{\text{trans}} = 89.73$ K.\footnote{Phase III then changes into phase I only at a 0.1 K higher temperature, at $T_{\text{trans}} = 89.83$ K, before melting at $T_{\text{fus}} = 90.35$ K occurs.\footnote{The metastable phase III was long undiscovered and was probably the cause for discrepancies in the melting and triple point temperatures of $\text{C}_2\text{H}_6$ determined from measurements of the enthalpy changes; the solid-solid phase transition from phase III to phase I was thought to be the melting of phase I.}}\cite{129,263}

For the metastable phase III a disordered orthorhombic structure was proposed by Braam and Vos using potential energy calculations.\footnote{Schutte et al. found from the NMR experiments that phase III must be an ordered solid and strongly disagreed with Braam and Vos's suggested disordered structure.\footnote{An orthorhombic structure was later confirmed through x-ray studies by Klimenko et al., who also supported the phase to be metastable since the orthorhombic structure was only observed upon heating and not upon cooling.}}\cite{265} Schutte et al. found from the NMR experiments that phase III must be an ordered solid and strongly disagreed with Braam and Vos's suggested disordered structure.\footnote{An orthorhombic structure was later confirmed through x-ray studies by Klimenko et al., who also supported the phase to be metastable since the orthorhombic structure was only observed upon heating and not upon cooling.\footnote{Please note, that in Pavese phase III and phase II relate to our phase II and phase III, respectively.}}\cite{129,264}

The possibility of the metastable phase IV of $\text{C}_2\text{H}_6$ at 45 K to be phase I is excluded here. The IR spectrum of phase I was observed in the aerosol spectrum as presented in Chapter 3, Fig. 3.5. The bands observed for phase I were: three peaks at 1470, 1465 and 1458 cm$^{-1}$ ($\nu_8$), two peaks at 1370 and 1365 cm$^{-1}$ ($\nu_6$), and six peaks at 824, 822, 820, 819, 816 and 814 cm$^{-1}$ ($\nu_9$) with weak signals possibly arising from small contributions of phase II $\text{C}_2\text{H}_6$. Phase I shows clear differences to the metastable phase IV at 45 K.

The metastable phase IV at 45 K could also be the metastable phase III found in the narrow temperature range of 89.73 to 83.83 K as described above. However, we have here no evidence to support this, and an IR spectrum of phase III close to the melting point has to our knowledge not been reported so far. Phase IV could also simply be another solid form of $\text{C}_2\text{H}_6$. According to Braam and Vos, an ordered orthorhombic structure of $\text{C}_2\text{H}_6$ that is stable at very low temperatures, could hypothetically exist.\footnote{Please note, that in Pavese phase III and phase II relate to our phase II and phase III, respectively.}
c) Solid Phase II of Ethane

In both cases, vapor deposition at 20 K and at 45 K, $\text{C}_2\text{H}_6$ crystallized into the stable phase II upon heating. The crystallization temperatures are 24 and 58 K, respectively. The spectrum of phase II crystallized from the amorphous phase at 24 K is shown in Fig. 7.1C with a triplet of the $\nu_8$ band at 1465, 1456, and 1450 cm$^{-1}$, a doublet of the $\nu_6$ band at 1370 and 1368 cm$^{-1}$, and a triplet of the $\nu_9$ band at 825.5, 816, and 813.5 cm$^{-1}$.

The spectrum of phase II crystallized from the metastable phase IV at 58 K (not shown) is almost identical: the band positions are slightly shifted by up to 0.5 cm$^{-1}$. The origin in this shift lies in the higher temperature. If both films are heated to 78 K, the IR spectra become identical in band shapes and positions. At 78 K (Fig. 7.1D) the peaks are shifted by up to 1 cm$^{-1}$ to higher frequencies compared to 24 K (except for the band at 825.5 cm$^{-1}$ which is shifted to a lower frequency). Furthermore, at 78 K, the $\nu_9$ band at 825.5 cm$^{-1}$ is slightly split into a doublet at 825 and 824 cm$^{-1}$ and the split of the $\nu_6$ doublet is not as pronounced as at 24 K. The spectrum of phase II of the thin film is in good agreement with literature.

Phase II can also be obtained by cooling the liquid phase below the melting point. Supercooling is not observed, most likely due to the influence of the substrate. Whereas the possibility to crystallize first in phase I exists, a fast and direct crystallization into phase II is observed. The narrow temperature range in which phase I is stable (89.83 K-90.35 K) and the fluctuation of the heating unit (± 1 K) make it more or less impossible to obtain phase I as a thin film in our experiment.

7.3.1.2 Identification of the Phases of the Aerosol Particles

Fig. 7.1E presents the IR spectrum of a film of liquid $\text{C}_2\text{H}_6$ just above the melting point, at 92 K. The spectrum of supercooled liquid $\text{C}_2\text{H}_6$ droplets at 78 K has previously been discussed in Chapter 3. For completeness and easier comparison with the thin film the spectrum of the $\text{C}_2\text{H}_6$ droplets is shown here again in Fig. 7.2B including the CH-stretching region around 3000 cm$^{-1}$. The IR spectra of the liquid film and supercooled droplets are in good agreement. The same is the case for the crystalline phase II, shown in Fig. 7.1D and Fig. 7.2A for thin film and aerosol particles, respectively. Fig. 7.2A is also once again an example for the slanted baseline caused by elastic scattering of light by particles > 100 nm in size.
Table 7.2: Observed vibrational frequencies of the phases of a thin film of C$_2$H$_6$ between 20-95 K

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Aerosol</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>78 K</td>
<td>78 K</td>
<td>20 K</td>
<td>45 K</td>
<td>24 K</td>
<td>78 K</td>
<td>92 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1485 (vw)</td>
<td>1471 (vw)</td>
<td>1487 (vw)</td>
<td>1485 (vw)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1463.1</td>
<td>1465.7</td>
<td>1461.3</td>
<td>1462.7</td>
<td>1456.2</td>
<td>1466.2</td>
<td>1461.5</td>
<td></td>
</tr>
<tr>
<td>1456.1</td>
<td>1450.8</td>
<td></td>
<td>1452.9</td>
<td>1456.3</td>
<td>1456.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1449.8</td>
<td>1451</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1370.6</td>
<td>1370.2</td>
<td>1369.1</td>
<td>1370</td>
<td>1370.3</td>
<td>1370.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1368.7</td>
<td>1368.4</td>
<td></td>
<td>1367.9</td>
<td>1369</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1364 (vw)</td>
<td>1364.8 (w)</td>
<td>1363.3 (vw)</td>
<td>1368 (sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1191.5 (vw)</td>
<td>819.5</td>
<td>816.6</td>
<td>821.1</td>
<td>825.4</td>
<td>825</td>
<td>819.1</td>
<td></td>
</tr>
<tr>
<td>817.1</td>
<td>814.3</td>
<td>816.9</td>
<td>813.4</td>
<td>816.9</td>
<td>816.9</td>
<td>814.2</td>
<td></td>
</tr>
</tbody>
</table>

[a] crystallized from the amorphous solid, [b] crystallized from the liquid, (vw): very weak, (w): weak, (sh): shoulder

7.3.2 Propane

The aerosol spectrum of C$_3$H$_8$ particles at 78 K has been discussed in Chapter 4.3.1. It was found that in the form of aerosol particles, C$_3$H$_8$ forms supercooled viscous liquid droplets which do not crystallize on the timescale of our experiment. This finding was supported by observations available from literature that state that C$_3$H$_8$ appears to be difficult to freeze.\textsuperscript{145,193,198} The possibility of forming amorphous particles was considered but excluded; the resolution of the only IR spectrum of a thin film of amorphous C$_3$H$_8$ in literature,\textsuperscript{195} that could support the formation of amorphous C$_3$H$_8$ particles, was too low for comparison with the aerosol spectrum.

Snyder and Schachtschneider described their thin film of C$_3$H$_8$ at 77.5 K as a viscous liquid whereas Coustenis et al.\textsuperscript{33,193} presented the spectrum of a crystalline film of C$_3$H$_8$ at 80 K.\textsuperscript{33,193} Both spectra slightly differ not only from each other but also from the aerosol spectrum. In this section we discuss the IR spectra of a thin film of C$_3$H$_8$ between 20-100 K with the goal of determining the IR spectra of the crystalline phases of C$_3$H$_8$ and comparing them with literature data and with the aerosol spectrum discussed in Chapter 4.3.1.
7.3.2.1 Thin Film IR Spectra of Propane

Fig. 7.3A-E presents the IR spectra of a thin film of C\textsubscript{3}H\textsubscript{8} between 20-100 K. Fig. 7.3A-C are the result of the vapor deposition of 3.5\% C\textsubscript{3}H\textsubscript{8} in He at 20 K and subsequent heating. Fig. 7.3D is the result of cooling a liquid film of C\textsubscript{3}H\textsubscript{8} (Fig. 7.3E) that formed after injection of C\textsubscript{3}H\textsubscript{8} gas into the optical cell at \(\sim\) 100 K. The peak positions of all observed phases of the thin film as well as of the viscous liquid aerosol particles are summarized in Table 7.3 and can be compared to the literature values of the viscous liquid film of Snyder and Schachtschneider and the crystalline film of Coustenis et al. in Chapter 4.3.1.1, Table 4.1.

a) Amorphous Propane

Deposition of C\textsubscript{3}H\textsubscript{8} at 20 K led to the formation of an amorphous film with broad bands. Absorption bands are found at 1465, 1454.5 (shoulder), 1383, 1368, 1361.5 (shoulder), 1331, 1186, 1155, 1051 919, 869, 820, and 746.5 cm\textsuperscript{-1}. The bands are mostly in agreement with the thin film studied at 4.2 K by Comeford and Gould except for a band at 1416 cm\textsuperscript{-1} that we do not observe.\textsuperscript{195} Furthermore, several of our bands are shifted up to 5 cm\textsuperscript{-1} compared to Comeford and Gould. The band at 820 cm\textsuperscript{-1} in Fig. 7.3A is caused by an C\textsubscript{2}H\textsubscript{6} impurity.

b) A Metastable Phase of Propane

C\textsubscript{3}H\textsubscript{8} has two solid phases, the stable phase \(\beta\) and metastable phase \(\alpha\), with \(T_{fus} = 85.5\) K and 81.2 K, respectively.\textsuperscript{145} Takeda et al. reported a glass transition temperature \(T_g = 45.5\) K and two solid-solid crystallization temperatures of \(T_{cryst} = 48.7\) K and \(T_{cryst} = 63.5\) K for vapor-deposited C\textsubscript{3}H\textsubscript{8} in DTA experiments.\textsuperscript{210}

We observed two crystallization temperatures that comply with Takeda et al. and that were found at \(\sim\) 46 K and \(\sim\) 65 K. Takeda et al. suggests that the second crystallization is “an irreversible transformation from an unidentified modification to the stable crystalline forms” and therefore identified the unidentified modification as a metastable form (from here on phase \(\gamma\)). That the second transition is irreversible was confirmed by cooling the sample back down to 55 K after crystallization at 65 K. The bands of the IR spectrum remained in the shape of the phase above 65 K.
Figure 7.3: IR spectra collected from a thin film of C3H8 between 20 and 100 K (A to E) and of supercooled viscous liquid C3H8 aerosol particles formed at 78 K (F). Spectra A to C were obtained by vapor deposition of C3H8 on a ZnSe substrate at 20 K followed by temperature increase. Spectra D and E were obtained by injecting C3H8 gas into an enclosed optical cell at 100 K and subsequent cooling. All spectra are baseline corrected except for the aerosol spectrum.

If the metastable phase γ is phase α or an unidentified crystalline phase cannot be clarified here. In literature, to the best of our knowledge, an IR spectrum of neither phase γ between 46 K < T < 65 K nor phase α close to its melting point has been reported and therefore spectra for comparison are not available. The IR spectrum of the metastable phase γ is presented in Fig. 7.3B.

b) Crystalline Phase β of Propane

The IR spectrum of the stable phase β, crystallized from the metastable phase γ is depicted in Fig. 7.3C and is in very good agreement with literature.33,193 Fig. 7.3C resembles the spectrum of Snyder and Schachtschneider closer than the one of Coustenis et al.33,193 Despite some minor differences it can be seen that C3H8 is in the same phase in all three spectra. The
differences could be mostly due to the resolution at which the spectra were recorded (Snyder and Schachtschneider: slit width 1-2 cm$^{-1}$, Coustenis et al.: 1 cm$^{-1}$, this work: 0.5 cm$^{-1}$).

Cooling down a liquid sample of C$_3$H$_8$ from 100 to 65 K results in immediate crystallization into phase $\beta$ at 65 K. This was unexpected since several references in literature state that the freezing of C$_3$H$_8$ occurred to be difficult$^{145,193}$ and that even with substantial supercooling as far as 25 K below the melting point freezing took several hours.$^{198}$ The reason for the “easy” crystallization from the liquid compared to literature could be either due to interactions with the substrate (ZnSe) or due to the ethane impurity as observed in the vapor-deposited film. However, the spectrum of the liquid film (Fig. 7.3E) and the spectrum of phase $\beta$ crystallized from the liquid (Fig. 7.3D) have no indication for the presence of ethane. This might be due to ethane having condensed to the coldest part of the cell which is not necessarily where the IR beam passes the sample.

The IR spectrum of the $\beta$ phase at 78 K obtained from freezing a liquid sample of C$_3$H$_8$ is shown in Fig. 7.3D. Interestingly, this spectrum does not resemble phase $\beta$ obtained from the solid-solid phase transition (Fig. 7.3C) by 100% as one would expect. The ratio between a number of bands appears to be different and the bands at 1452, 1049, and 917 cm$^{-1}$ are almost entirely missing. The sample was molten and refrozen several times with the same result. No contribution from the metastable phase $\gamma$ in both spectra of the crystallized phase $\beta$ (obtained from vapor deposition and liquid deposition) was found. Any further attempt to explain this observation remained in vain.

According to Pavese and Besley “the greater the degree of supercooling of the liquid, the more likely it was that the higher-melting-temperature solid would appear.”$^{145}$ Therefore, the IR spectra presented in Fig. 7.3C and D are declared to be the stable phase $\beta$ and not the metastable phase $\alpha$ particularly since Pavese and Besley also discovered that cooling phase $\alpha$ more than 1.5 K below its freezing temperature would result in transformation into phase $\beta$.$^{145}$

### 7.3.2.2 Identification of the Phase of the Aerosol Particles

The aerosol spectrum of C$_3$H$_8$ is presented in Fig. 7.3F. Comparing the aerosol spectrum with the solid and liquid phases of the thin film spectra (Figs. 7.3A-E) indicates that the aerosol spectrum can only be amorphous (Fig. 7.3A) or liquid (Fig. 7.3E). A closer comparison shows
Table 7.3: Observed vibrational frequencies of the phases of a thin film of C$_3$H$_8$ between 20-100 K and viscous liquid aerosol particles at 78 K

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Thin Film</th>
<th>Aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>Metastable</td>
<td>Crystalline$^a$</td>
<td>Crystalline$^b$</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>20 K</td>
<td>46 K</td>
<td>78 K</td>
<td>78 K</td>
<td>100 K</td>
<td>78 K</td>
</tr>
<tr>
<td>1477.1</td>
<td>1472.1</td>
<td>1472.1</td>
<td>1469</td>
<td>1469.5</td>
<td></td>
</tr>
<tr>
<td>1465.4</td>
<td>1460.8</td>
<td>1461.2</td>
<td>1461.1</td>
<td>1465.2</td>
<td>1466.1</td>
</tr>
<tr>
<td>1457.6</td>
<td>1457.6</td>
<td>1456 (sh)</td>
<td>1456.5 (sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1452.2</td>
<td>1448.5 (w)</td>
<td>1448 (w)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1442.7</td>
<td>1440 (vw)</td>
<td>1440 (vw)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1388.5</td>
<td>1388.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1383.2</td>
<td>1382.6</td>
<td>1383.2 (vw)</td>
<td>1382.8 (vw)</td>
<td>1383.9</td>
<td>1384.2</td>
</tr>
<tr>
<td>1371.1</td>
<td></td>
<td>1369.5 (sh)</td>
<td>1369.7</td>
<td>1368.8</td>
<td>1369.1</td>
</tr>
<tr>
<td>1367.8</td>
<td></td>
<td>1367.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1361 (sh)</td>
<td>1363.6</td>
<td>1362.3 (sh)</td>
<td>(1362.2 (sh))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1335 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1331.1</td>
<td>1330 (vw)</td>
<td>1331.2 (w)</td>
<td>1333.6</td>
<td>1332.6</td>
<td></td>
</tr>
<tr>
<td>1329.9 (w)</td>
<td>1329.9 (w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1320 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1297 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1288 (vw)</td>
<td></td>
<td></td>
<td></td>
<td>(1288.4)</td>
<td></td>
</tr>
<tr>
<td>1185.8</td>
<td>1187 (vw)</td>
<td>1185.3</td>
<td>1185.3</td>
<td>1186.2</td>
<td>1186.5</td>
</tr>
<tr>
<td>1179.5 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1178.9 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1155.1</td>
<td>1156.9</td>
<td>1155.6</td>
<td>1155.6</td>
<td>1155.3</td>
<td>1155.4</td>
</tr>
<tr>
<td>1141.5 (vw)</td>
<td></td>
<td>1137 (w)</td>
<td>1137 (vw)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1055.5</td>
<td></td>
<td></td>
<td>1055 (vw)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1050.8</td>
<td>1049 (w)</td>
<td>1049.1</td>
<td>1048 (vw)</td>
<td>1050.9</td>
<td>1050.8</td>
</tr>
<tr>
<td>1046 (vw)</td>
<td>1043.4 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1038 (vw)</td>
<td>1035.4 (vw)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>919.4</td>
<td>923</td>
<td>921 (w)</td>
<td>921 (vw)</td>
<td>919.6</td>
<td>919.6</td>
</tr>
<tr>
<td>914.1</td>
<td>917.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>899.5 (vw)</td>
<td>894.5 (vw)</td>
<td>898.9 (vw)</td>
<td>898.7 (vw)</td>
<td>900 (vw)</td>
<td>(900)</td>
</tr>
<tr>
<td>869</td>
<td>872.3</td>
<td>867.4</td>
<td>867.4</td>
<td>869.2</td>
<td>869.5</td>
</tr>
<tr>
<td>862 (vw)</td>
<td>860.6 (vw)</td>
<td></td>
<td></td>
<td>(861.9 (sh))</td>
<td></td>
</tr>
<tr>
<td>746.1</td>
<td>748.1</td>
<td>746.6</td>
<td>746.4</td>
<td>746.6</td>
<td>746.9</td>
</tr>
</tbody>
</table>

$^a$crystallized from the metastable solid, $^b$crystallized from the liquid, (vw): very weak, (w): weak, (sh): shoulder, (): only at high concentrations
that the aerosol spectrum is identical to the liquid thin film in the fingerprint region and that both are very similar to the amorphous spectrum. The absorption bands of the amorphous film are broadened compared to the liquid and the band at \( \sim 1465 \, \text{cm}^{-1} \) experiences two shoulders at \( \sim 1470 \) and \( 1455 \, \text{cm}^{-1} \) in the liquid and aerosol spectrum whereas the first one is missing and the second one is less pronounced in the amorphous spectrum. Therefore, we can conclude that the phase we observe for \( \text{C}_3\text{H}_8 \) aerosol particles under our experimental conditions is indeed liquid (supercooled).

### 7.3.3 \( n \)-Pentane

The phase behavior of \( n \)-C\(_5\)H\(_{12} \) aerosol particles at 78 K and in N\(_2\) as bath gas was discussed in Chapter 4.3.2. The phase after particle formation was identified to have a disordered structure and to be either of a supercooled liquid or more likely of an amorphous solid. Previously, for comparison and identification we measured an ATR IR spectrum of bulk liquid \( n \)-C\(_5\)H\(_{12} \) at room temperature and the absorption IR spectrum of the liquid phase at 153 K was available from Snyder\(^{216}\). At room temperature the bands are broad and the ratio of \( \text{trans-trans} \) (TT) to \( \text{trans-gauche} \) (TG) conformers is most likely different compared to lower temperatures. Salam and Deleuze determined the fractions of TT, TG, and \( \text{gauche-gauche} \) (GG) in the gas phase to be 0.282, 0.673, and 0.045, respectively \((T = 298.15 \, \text{K})\) and only once below 170 K the TT conformer was to become the dominant species\(^{267}\). The liquid spectrum reported by Snyder\(^{216}\) looked similar to the spectrum of \( n \)-C\(_5\)H\(_{12} \) after particle formation with minor differences\(^{216}\). This made it difficult to clarify if the particles were liquid or a disordered solid upon formation. However, we assumed that most likely a disordered solid was formed since the survival of supercooled \( n \)-C\(_5\)H\(_{12} \) particles at 78 K (65 K below the freezing point) is unlikely. The determination of the IR spectra of the phases of a thin film of \( n \)-C\(_5\)H\(_{12} \) between 20-150 K (Fig. 7.4A-E) should help to clarify what phase \( n \)-C\(_5\)H\(_{12} \) particles are in after formation (Fig. 7.5A).
7.3.3.1 Thin Film IR Spectra of \( n \)-Pentane

Fig. 7.4A-E presents the IR spectra of a thin film of \( n \)-C\(_5\)H\(_{12}\) between 20-150 K, and an ATR spectrum of \( n \)-C\(_5\)H\(_{12}\) at room temperature (293 K).

\( a) \) Amorphous \( n \)-Pentane

Vapor deposition of pure \( n \)-C\(_5\)H\(_{12}\) at 20 K led to the formation of a thin film with amorphous structure (Fig. 7.4A). It can be seen that the band shapes and relative intensities of the amorphous structure are similar to the band shapes of the liquid spectrum at 150 K (Fig. 7.4E) indicating that vapor deposition captures the ratio of the \( TT \) and \( TG \) conformers in the liquid (see Section 4.3.2 and Table 4.2 for isomers). Increasing the temperature leads to conversion of \( TG \) into \( TT \) isomers if the added energy is high enough to cross the rotational barrier (C-C torsional barrier \( \sim 2.8 \) kcal mol\(^{-1}\)).\(^{268}\) In the spectrum this results in a decrease in the intensity of the bands attributed to the \( TG \) isomer and an increase in the intensity of the bands attributed to the \( TT \) isomer.

At 45 K (Fig. 7.4B) several bands have disappeared (1307, 1075, 1012, 986, 897, 861, and 839 cm\(^{-1}\)), or significantly decreased (1342, 1138, 908, and 762 cm\(^{-1}\)) or increased (1471, 1455, 1367, 1180, 1146, 1066, 1038, 1026, 920, 867, 857, and 727 cm\(^{-1}\)) in intensity compared to the amorphous structure. We call this phase “amorphous-annealed”. With amorphous-annealed we mean here an amorphous structure of \( n \)-C\(_5\)H\(_5\) that shows partially transformation of bands attributed to the \( TG \) isomer into the \( TT \) isomer compared to the amorphous structure initially formed at 20 K, after the sample was exposed to a higher temperature for a period of time (here 45 K for 5 min). Comparing these observations to literature data as presented in Chapter 4.3.2, Table 4.2, the bands of decreased and increased intensities can indeed be assigned to the \( TG \) and \( TT \) isomers, respectively.\(^{193,214}\)

\( b) \) Crystalline \( n \)-Pentane

At 70 K, the vapor-deposited film of \( n \)-C\(_5\)H\(_{12}\) crystallized with all molecules in the \( TT \) form.\(^{196,215}\) The transition took about 45 minutes to complete and IR spectra were recorded every 5 minutes. The crystallization temperature observed is in compliance with Takeda et al.
Figure 7.4: IR spectra collected from a thin film of \(n\)-C\(_5\)H\(_{12}\) between 20 and 115 K. Spectra A to C were obtained by vapor deposition of \(n\)-C\(_5\)H\(_{12}\) gas on a ZnSe substrate at 20 K followed by temperature increase. Spectra D and E were obtained by injecting \(n\)-C\(_5\)H\(_{12}\) gas into an enclosed optical cell at \(\sim\) 200 K and subsequent cooling. Spectrum F is the bulk liquid measured at room temperature with an ATR FTIR. Spectra A to E are baseline corrected.

who found a \(T_{\text{cryst}} = 71.8\) K for vapor-deposited \(n\)-C\(_5\)H\(_{12}\) as part of DTA measurements.\(^{210}\)

The spectrum of the crystallized film is shown in Fig. 7.4C, at 78 K. It is in good agreement with the spectrum of Snyder and Schachtschneider except for the bands at 1336, 1303, and 966 cm\(^{-1}\), that are missing here.\(^{193}\) 1336 and 1303 cm\(^{-1}\) can be attributed to the \(GG\) and \(TG\) isomers, respectively, that might have not fully converted into the \(TT\) form in the spectrum of Snyder and Schachtschneider.

The liquid sample of \(n\)-C\(_5\)H\(_{12}\) crystallized just below the melting point and was then cooled down to 78 K for comparison with the aerosol spectrum at 78 K. Interestingly, the IR spectrum of the thin film of \(n\)-C\(_5\)H\(_{12}\) crystallized from the liquid (Fig. 7.4D) appears to be slightly different from the one obtain via heating a sample of a vapor-deposited film. The same
Figure 7.5: Observed phases of $n$-C$_5$H$_{12}$ aerosol particles at 78 K in N$_2$ as bath gas. A: Crystal phase in all-trans configuration. The crystal phase of the aerosols fits the crystal phase of the thin film obtained from the amorphous structure (Fig. 7.4C) best. B: Disordered phase that forms immediately after particle formation. The disordered aerosol phase fits the amorphous-annealed phase at 45 K of the thin film (Fig. 7.4B) best.

observation was made earlier for the thin films of C$_3$H$_8$ (Section 7.3.2). The crystalline film obtained from the liquid is missing the bands at 1467.5, 1455, 1297, and 727 cm$^{-1}$ and has significantly lower intensities at 1364, 1026 and 921 cm$^{-1}$. The $TT$ and $TG$ conformers as well as IR and Raman activity of these bands were considered as an explanation. However, all bands are attributable to the $TT$ isomer except for the band at 1026 cm$^{-1}$ which is attributable to $TT$ and $TG$. Furthermore, all bands are either IR active or IR and Raman active.

7.3.3.2 Identification of the Phases of the Aerosol Particles

The obtained spectra of the thin film of $n$-C$_5$H$_{12}$ between 20-150 K can be used to compare the IR spectrum of the disordered phase of $n$-C$_5$H$_{12}$ aerosol particles after formation in N$_2$ as bath gas. The spectrum of the disordered particle phase is shown in Fig. 7.5B. Comparing this spectrum to the thin film phases in Fig. 7.4A-E one can determine that the amorphous-annealed structure at 45 K fits the aerosol spectrum best. Therefore, the previous speculation that $n$-C$_5$H$_{12}$ aerosol particles form most likely a disordered solid and not a supercooled liquid is confirmed.
The crystalline structure of \( n\)-C\(_5\)H\(_{12}\) aerosol particles in Fig. 7.5A is also compared to the crystalline structures presented in Figs. 7.4C and D. The aerosol spectrum is in agreement with the crystalline structure in Fig. 7.4C, the structure obtained from the crystallization of the amorphous-annealed phase.

7.4 Conclusions

We have studied the thin films of C\(_2\)H\(_6\), C\(_3\)H\(_8\), and \( n\)-C\(_5\)H\(_{12}\) between 20 K and their respective melting points using IR spectroscopy. For C\(_2\)H\(_6\) two crystalline phases were found depending on the deposition temperature. Deposition at 20 K led to the formation of an amorphous phase that crystallized into the stable phase II at 24 K, and deposition at 46 K resulted in a crystalline metastable phase (phase IV) that crystallized into phase II at \( \sim \) 58 K. Comparing the thin film spectrum to the aerosol spectrum of the liquid phase and the solid phase II shows that in both cases thin film and aerosol spectrum are identical.

Propane was deposited at 20 K as an amorphous solid and experienced two solid-solid phase transitions at \( \sim \) 46 K and \( \sim \) 65 K. The first transition resulted in a metastable phase (phase \( \gamma \)) that crystallized into the stable phase \( \beta \) upon heating. The stable phase \( \beta \) was found to be consistent with literature. Comparison of the IR spectrum of aerosol particles and thin films confirmed that C\(_3\)H\(_8\) aerosol particles are (supercooled) viscous liquid droplets at 78 K and under the conditions and timescale of our experiment.

After deposition at 20 K and heating the sample to 45 K the thin film of \( n\)-C\(_5\)H\(_{12}\) has changed from an amorphous structure to an amorphous-annealed structure. The amorphous-annealed structure was found to be the best fit for the spectrum of \( n\)-C\(_5\)H\(_{12}\) aerosol particles after particle formation at 78 K in N\(_2\) as bath gas. Therefore, the thin film measurements confirmed what was previously assumed that \( n\)-C\(_5\)H\(_{12}\) does not form supercooled liquid droplets but rather unstructured solid particles at 78 K.
Chapter 8

Conclusion

8.1 Summary and Conclusions

This thesis presents laboratory studies of the phase behavior of short-chained hydrocarbon aerosols (C$_2$-C$_5$) under conditions relevant for the atmosphere of Saturn’s moon Titan using infrared (IR) extinction spectroscopy. These types of data are essential for atmospheric models of Titan, such as those discussed by Barth and Toon and Lavvas et al.\textsuperscript{82,94} Furthermore, the mid-infrared spectra obtained for the liquid phase and a range of solid phases for each substance can be used as reference data for astronomical remote sensing applications.

In Chapter 3 it is demonstrated that supercooled liquid ethane (C$_2$H$_6$) aerosols can indeed form under conditions similar to those in Titan’s lower atmosphere, where C$_2$H$_6$ aerosols and C$_2$H$_6$ clouds are thought to play an important role ($T \sim 78$ K, $p \sim 560$ mbar, altitude $\sim 18$ km). The C$_2$H$_6$ droplets are substantially stabilized against freezing by the incorporation of methane (CH$_4$) gas into the droplets. The higher the methane mole fraction in the gas phase ($y_{CH_4}$) the longer the delay of the onset of freezing of the supercooled droplets. One possible explanation for this observation is that at larger $y_{CH_4}$ more methane is incorporated into the droplets. A higher methane content in the droplets results in an increased freezing point depression and a decreased degree of supercooling, thus extending the lifetime of the supercooled phase.

For these droplets a composition of $\sim 20\%$ CH$_4$ and $\sim 80\%$ C$_2$H$_6$ was estimated, potentially with a small N$_2$ contribution.\textsuperscript{183} A quantitative spectroscopic evaluation of the droplet composition is not possible since the rotational-vibrational bands of gas-phase CH$_4$ are strong
and overlap with the bands of CH$_4$ in the liquid phase so that the CH$_4$ content in the liquid phase could not be detected. Monte-Carlo (MC) simulations and an empirical equation of state model (EOS) provide computational methods to determine droplet compositions. Luckhaus et al. showed that for the binary system CH$_4$-C$_2$H$_6$ the amount of CH$_4$ incorporated into C$_2$H$_6$ droplets indeed increases with increasing $y_{CH_4}$. The same trend was found for the ternary system CH$_4$-C$_2$H$_6$-N$_2$. In the case of the ternary system not only CH$_4$ is incorporated, but also a small amount of N$_2$ which also increases with increasing $y_{CH_4}$. The MC and EOS calculations also reveal that ternary CH$_4$-C$_2$H$_6$-N$_2$ droplets form below an altitude of 7 km and above 30 km. Between 7-30 km the amount of C$_2$H$_6$ in CH$_4$-N$_2$ droplets is negligible and these droplets can be modeled to a good approximation by the binary system CH$_4$-N$_2$. The droplet composition in Titan’s lower atmosphere as determined by the EOS model is presented in Fig. 8.1.

The experimental studies show that C$_2$H$_6$ can form supercooled liquid droplets under conditions mimicking Titan’s troposphere ($T = 78$ K, $p \sim 550$ mbar) that are long-lived. These particles are stabilized against freezing by the incorporation of CH$_4$ and N$_2$ gas. The fact that supercooled droplets are not merely transient species might have important implications for the nucleation and condensation of CH$_4$ in Titan’s atmosphere. Previously, C$_2$H$_6$ was
assumed to form solid particles and supercooled liquid droplets were not considered.\textsuperscript{114,125} For the condensation of CH\textsubscript{4}, liquid C\textsubscript{2}H\textsubscript{6} particles might be better CCN than solid C\textsubscript{2}H\textsubscript{6} particles due to the miscibility of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} in the liquid phase. The liquid particles furthermore have different optical properties compared to solid particles, which could thus affect Titan’s radiation budget. Therefore, as previously suspected by Barth and Toon,\textsuperscript{82} supercooled droplets cannot be neglected and the metastable supercooled state should be incorporated into cloud microphysical models.

The phase behavior of propane (C\textsubscript{3}H\textsubscript{8}), n-butane (n-C\textsubscript{4}H\textsubscript{10}) and n-pentane (n-C\textsubscript{5}H\textsubscript{12}) aerosols is discussed in Chapters 4 and 5. C\textsubscript{3}H\textsubscript{8} aerosols are found to form long-lived supercooled liquid droplets as in the case of C\textsubscript{2}H\textsubscript{6} aerosols. The onset of freezing could not be observed on the time scale of the experiments and the particles remained liquid during the whole observation time. According to Tan et al., C\textsubscript{3}H\textsubscript{8} condenses at an altitude around 63 km in Titan’s atmosphere and forms liquid droplets containing \textasciitilde 1.57\% C\textsubscript{2}H\textsubscript{6}.\textsuperscript{269} The C\textsubscript{3}H\textsubscript{8} content of these droplets decreases with decreasing altitudes due to increasing dissolution of other atmospheric components (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}).\textsuperscript{269} These findings show that in Titan’s lower stratosphere liquid multi-component clouds, the composition of which depends on the altitude, might exist. These cloud condensates could influence the nucleation of methane and ethane and other atmospheric species.

n-C\textsubscript{5}H\textsubscript{12} has a much higher freezing point than C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} and therefore has a different phase behavior. Under Titan conditions (p, T), n-C\textsubscript{5}H\textsubscript{12} aerosol particles crystallize immediately upon formation in He bath gas. In N\textsubscript{2} bath gas, on the other hand, n-C\textsubscript{5}H\textsubscript{12} aerosol particles first form an amorphous-annealed solid before crystallization.

Such a difference in the phase behavior upon particle formation in He and N\textsubscript{2} bath gases was not observed for n-C\textsubscript{4}H\textsubscript{10} despite its fairly high melting point compared to that of C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8}. The initial phase of n-C\textsubscript{4}H\textsubscript{10} aerosols after formation is amorphous-annealed in both He and N\textsubscript{2} bath gas, followed by a phase transition to solid crystalline phase II n-C\textsubscript{4}H\textsubscript{10}. A dependence in the time-evolution of the recorded spectra on the type of bath gas was noticed during the subsequent transition from solid phase II to solid phase III. Particle re-crystallization was slower in He than in N\textsubscript{2}. This difference is attributed to the particle
size since larger particles form in N₂ and not to a difference in freezing kinetics.

C₄H₁₀ and C₅H₁₂ have so far not been detected in Titan’s atmosphere. However, both species could be involved in cloud processes on Titan, for example by contributing to the coating of haze particles. C₄H₁₀ gas is estimated to be present at ∼ 200 ppbv and is expected to condense and coat haze particles at an altitude ∼ 68 km (T ∼ 108 K), which then act as CCN for other hydrocarbons.¹⁰⁸ At this temperature pure n-C₄H₁₀ forms the disordered solid phase I and undergoes a phase transition to phase II and III when the particles reach lower altitudes and thus lower temperatures. Therefore, if n-C₄H₁₀ and n-C₅H₁₂ exist and condense in Titan’s atmosphere, the condensed phase will most likely only exist in the solid state even for mixed systems.

For the observed phase transitions of n-C₄H₁₀ and n-C₅H₁₂ aerosols the freezing kinetics were evaluated and the surface and volume nucleation rate constants J_S and J_V determined using a Mie model in conjunction with a non-linear fit. In the case of the long-lived binary and ternary droplets (CH₄-C₂H₆ and CH₄-C₂H₆-N₂) the achievable experimental observation times are too short to determine accurate freezing rate constants. In the case of C₃H₈ aerosols no phase transition is observed. The analysis of the freezing kinetics for n-C₄H₁₀ and n-C₅H₁₂ aerosols is limited by the accuracy in the determination of the particle size distribution, which depends on the complex refractive index data. The complex refractive index of solid n-C₄H₁₀ and n-C₅H₁₂ have so far not been reported in literature and the complex refractive index of liquid n-C₅H₁₂ was used instead. The obtained nucleation rate constants are summarized in Table 8.1. The uncertainty amounts to about one order of magnitude. The table also contains the freezing rate constants for supercooled C₂H₆ droplets determined by Sigurbjörnsson and Signorelli.¹¹¹

It should be noted that a simple nucleation model was found to be insufficient to properly describe the crystallization of n-C₄H₁₀ particles from amorphous-annealed to solid phase II and to describe the crystallization of n-C₅H₁₂ aerosols in N₂ bath gas. It is assumed that N₂ is incorporated into the amorphous-annealed phase and needs to be expelled first before crystallization can occur thus altering the type of kinetics. This explanation holds for n-C₅H₁₂ but not for n-C₄H₁₀ where no difference of the phase behavior in He or N₂ bath gas
Table 8.1: Nucleation rate constants for hydrocarbon aerosols at 78 K

<table>
<thead>
<tr>
<th>Alkane</th>
<th>$J_V$ (cm$^{-3}$ s$^{-1}$)</th>
<th>$J_S$ (cm$^{-2}$ s$^{-1}$)</th>
<th>Bath gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane[a]</td>
<td>$10^7$-10$^9$</td>
<td>$10^3$-10$^5$</td>
<td>He, N$_2$</td>
</tr>
<tr>
<td>Propane</td>
<td>N/A</td>
<td>N/A</td>
<td>He, N$_2$</td>
</tr>
<tr>
<td>n-Butane (a)</td>
<td>$10^{12}$-10$^{14}$</td>
<td>$10^{13}$-10$^{15}$</td>
<td>He, N$_2$</td>
</tr>
<tr>
<td>n-Butane (b)</td>
<td>$10^9$-10$^{11}$</td>
<td>$10^{11}$-10$^{13}$</td>
<td>He, N$_2$</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>$10^{11}$-10$^{13}$</td>
<td>$10^{12}$-10$^{14}$</td>
<td>N$_2$</td>
</tr>
</tbody>
</table>

[a] Sigurbjörnsson and Signorelli, 111, (a) 1st transition, (b) 2nd transition

is observed, suggesting that N$_2$ is not incorporated into $n$-C$_4$H$_{10}$ aerosol particles. $n$-C$_4$H$_{10}$ aerosol particles instead might undergo a two-step process or a “zonal” crystallization.

The freezing of C$_2$H$_6$, C$_3$H$_8$, $n$-C$_4$H$_{10}$, and $n$-C$_5$H$_{12}$ aerosols was also studied in the presence of acetylene (C$_2$H$_2$), carbon dioxide (CO$_2$), and water (H$_2$O) aerosols as ice-nuclei (IN)(heterogeneous freezing). C$_2$H$_2$, CO$_2$, and H$_2$O are expected to condense in Titan’s lower atmosphere and therefore can serve as condensation and freezing nuclei for the above hydrocarbons and for other condensable species. 33,133

The presence of solid trace aerosols significantly accelerates crystallization of supercooled C$_2$H$_6$, C$_2$H$_6$-CH$_4$, and C$_2$H$_6$-CH$_4$-N$_2$ droplets, and of $n$-C$_4$H$_{10}$ and $n$-C$_5$H$_{12}$ aerosol particles. The C$_2$H$_6$-CH$_4$ and C$_2$H$_6$-CH$_4$-N$_2$ still remain long-lived further reinforcing the importance of the supercooled phase in Titan’s atmosphere. In the case of C$_3$H$_8$ aerosol particles even the presence of trace aerosols could not initiate freezing. Therefore C$_3$H$_8$ aerosols have a strong tendency to remain in the liquid state even in the presence of heterogeneous nuclei. This is important, since C$_3$H$_8$ is expected to condense on Titan near an altitude of about 63 km together with other substances such as C$_2$H$_2$. 33,269

With a minimum temperature of 71 K in Titan’s lower atmosphere, it is plausible that C$_3$H$_8$ exists mainly as a (supercooled) liquid over extended atmospheric regions. Thus, C$_3$H$_8$ droplets could substantially influence the condensation and phase behavior of CH$_4$ and C$_2$H$_6$.

Furthermore, the ice-nucleating effectiveness of C$_2$H$_2$, CO$_2$, and H$_2$O particles has been discussed and compared for supercooled C$_2$H$_6$ droplets, and for $n$-C$_4$H$_{10}$ and $n$-C$_5$H$_{12}$ aerosol particles. The observed differences were rationalized in terms of the solid structure (i.e. crystalline, polycrystalline) of the IN. C$_2$H$_2$ aerosols are the more effective IN, attributed to the
The fact that they have a flexible crystal structure and a less ordered surface structure than CO\textsubscript{2} particles. H\textsubscript{2}O aerosols are the least effective IN. The influence of nuclei composition on the effectiveness of heterogeneous nucleation is an important aspect in understanding cloud processes.\textsuperscript{182}

The first experimental investigation of the influence of different freezing mechanisms (immersion and contact freezing) on the rate of heterogeneous crystallization under conditions relevant to Titan has been performed. Using C\textsubscript{2}H\textsubscript{2} as IN both mechanisms can spectroscopically be distinguished due to the characteristic spectroscopic features of polycrystalline and orthorhombic C\textsubscript{2}H\textsubscript{2}.\textsuperscript{161} In the case of contact freezing, C\textsubscript{2}H\textsubscript{2} is observed in the polycrystalline form only. Both freezing mechanisms are possible on Titan. Which one actually occurs depends on CCN concentration and supersaturation of the condensable phase.

The determination of the kinetics for heterogeneous crystallization from the experimental data obtained is, at this point, not possible. The rate of heterogeneous nucleation depends strongly on the nuclei size distribution and concentration. However, the size distribution and concentration of IN cannot be determined accurately with the current experimental set-up because the IN particles are too small (< 100 nm in diameter).

In summary, the study of the homogeneous and heterogeneous phase behavior of hydrocarbon aerosols presented in this thesis provides a detailed picture of the freezing behavior of these aerosols under conditions relevant to Titan. The phase of aerosols affects their optical properties which in turn influence absorption and scattering behavior and thus the radiation balance of Titan’s atmosphere. Several of the described findings in this thesis should be considered in microphysical and chemical atmospheric models. The provided nucleation rate constants for the homogeneous crystallization of \textit{n}-C\textsubscript{4}H\textsubscript{10} and \textit{n}-C\textsubscript{5}H\textsubscript{12} can be incorporated into models. In addition, infrared extinction spectra of all studied hydrocarbons aerosols and their observed phases have been reported between 3500-650 cm\textsuperscript{-1} and some were made available as reference data for astronomical remote sensing applications.\textsuperscript{260}
8.2 Future Directions

Several questions have not been addressed in this thesis due to experimental limitations. This includes the determination of the composition and the quantitative description of the freezing kinetics of the mixed supercooled CH$_4$-C$_2$H$_6$-N$_2$ droplets, the quantitative study of the heterogeneous crystallization kinetics, and the determination of the nucleation rate constants as a function of temperature. The determination of the composition of binary and ternary droplets is currently limited to theoretical studies as described by Firnescu et al., Luckhaus et al., and Tan et al.

Currently efforts are being made to develop an alternative experimental approach to overcome some experimental limitations: The development of an optical trap to study single aerosol particles at cryogenic temperatures under a variety of conditions (e.g. temperatures, pressures, atmospheric composition, and relative humidity). With the optical trap experimental timescales of hours to days can be achieved, allowing the long-term observation of the trapped aerosol particle. Thus the observation and quantitative description of the kinetics of the freezing of supercooled C$_3$H$_8$ and mixed supercooled CH$_4$-C$_2$H$_6$-N$_2$ droplets might become possible. Furthermore, the optical trap allows for the determination of the size of the trapped aerosol droplet/particle opening up a method for the determination of the size distribution of heterogeneous crystallization nuclei. Furthermore, for the study of heterogeneous crystallization a better understanding of the nuclei and nuclei-substrate interactions is needed. This would involve, amongst other things, the determination of surface tensions, contact angles, and surface structures. To improve the accuracy of the determined freezing rate constants complex refractive index data for the solid phases of C$_3$H$_8$, n-C$_4$H$_{10}$, and n-C$_5$H$_{12}$ are needed. These data can be obtained from thin film measurements.

Studies of liquid multi-component systems are also of interest to gain insight into the composition of lakes and surface deposits on Titan, which are not well known. The composition of Titan’s lakes is currently based on modeling and has been estimated by Cordier et al. and Tan et al. However, the composition has been found to be highly sensitive to the thermodynamic data and the overall C$_2$H$_6$ atmospheric mole fraction used in the model. Therefore the experimental study of multi-component systems focused on the dependence
of their composition on the gas phase composition and the determination of more accurate thermodynamic data would be of interest.
Bibliography


Appendix A

Addition to Chapter 2: Experimental

A.1 Optical Path Length Calibration

The optical path length is the total length the light travels through the cell and depends on
the number of times the light is reflected on the White optics. It is not simply a multiplication
of the geometrical path length due to reflection, scattering, and absorption losses by windows,
mirrors and bath gas. The optical path length can be determined using a known dilution of
N$_2$O in He or N$_2$.

A dilution of 1 % N$_2$O in N$_2$ was injected into the evacuated cooling cell ($T = 293$ K) with
a backing pressure of 1000 mbar. The injected sample was further diluted with N$_2$ to 800 mbar
resulting in $\sim 0.013\%$ N$_2$O. The cell path length was varied from 4 to 32 in steps of 4. For
each path length an IR spectrum was recorded.

Table A.1 provides the vibrational bands of N$_2$O and includes transition dipoles $\mu$ and band
strengths $S$.\textsuperscript{270} Using Eqs. A.1 to A.5 the information provided in Table A.2 and knowledge
of the N$_2$O concentration in the cell, the optical path length in dependence on the number
of passes can be calculated (vibrational bands of N$_2$O marked with a * were used for the
calculation of the path length).

\textbf{Lambert-Beer Law}

\[
\ln \left( \frac{I_0}{T} \right) = \sigma \cdot c \cdot l
\]
Table A.1: \( \text{N}_2\text{O} \) vibrational bands, dipole moments and band strengths

<table>
<thead>
<tr>
<th>Band</th>
<th>( \text{cm}^{-1} )</th>
<th>( \mu ) (debyes)[^a]</th>
<th>( S ) (cm(^2) atm(^{-1}))[^a]</th>
<th>( S ) (cm mol(^{-1}))[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_2 )</td>
<td>589</td>
<td>0.069</td>
<td>28.9(1.5)</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_2 )</td>
<td>1168</td>
<td>0.0262</td>
<td>8.27(43)</td>
<td></td>
</tr>
<tr>
<td>( \nu_1^* )</td>
<td>1285</td>
<td>0.130</td>
<td>225(12)</td>
<td>5.5535\times10^6</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>2224</td>
<td>0.249</td>
<td>1421(76)</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_1^* )</td>
<td>2563</td>
<td>0.0348</td>
<td>32.1(1.7)</td>
<td>7.7803\times10^5</td>
</tr>
<tr>
<td>( 3\nu_1 )</td>
<td>3836</td>
<td>0.00684</td>
<td>1.85(18)</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_3 )</td>
<td>4417</td>
<td>0.00579</td>
<td>1.53(15)</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + 2\nu_2^* )</td>
<td>2462</td>
<td>0.0170</td>
<td>7.35(38)</td>
<td>1.7835\times10^5</td>
</tr>
<tr>
<td>( \nu_2 + \nu_3 )</td>
<td>2798</td>
<td>0.00881</td>
<td>2.24(13)</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_2 + \nu_3 )</td>
<td>3364</td>
<td>0.00798</td>
<td>2.21(13)</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + \nu_3^* )</td>
<td>3481</td>
<td>0.0361</td>
<td>46.8(2.4)</td>
<td>1.1371\times10^6</td>
</tr>
<tr>
<td>( 2\nu_1 + 2\nu_2 )</td>
<td>3749</td>
<td>0.00425</td>
<td>0.70(7)</td>
<td></td>
</tr>
</tbody>
</table>

\[^a\]Kagann\(^{270}\), \[^b\]from Eq. A.3

Remarks: *bands used for integration; \( \nu_2 \) is a double degenerate band

Band strength \( S \) (cm mol\(^{-1}\)) by integration

\[
S = \frac{1}{c \cdot l} \int_{\tilde{\nu}_{\text{min}}}^{\tilde{\nu}_{\text{max}}} \ln \left( \frac{I_0}{I} \right) d\tilde{\nu}
\]  \hspace{1cm} (A.2)

Band strength \( S \) (cm mol\(^{-1}\)) using the transition dipole \( \mu \)

\[
S = 2.50664 \cdot 10^5 \cdot |\mu|^2 \cdot \tilde{\nu}_0
\]  \hspace{1cm} (A.3)

Optical path length (cm)

\[
l = \frac{1}{S \cdot c_{\text{cell}}} \ln(10) \int_{\tilde{\nu}_{\text{min}}}^{\tilde{\nu}_{\text{max}}} \log \left( \frac{I_0}{I} \right) d\tilde{\nu}
\]  \hspace{1cm} (A.4)

Concentration (mol cm\(^{-3}\))

\[
c_{\text{cell}} = \frac{1}{S \cdot l} \ln(10) \int_{\tilde{\nu}_{\text{min}}}^{\tilde{\nu}_{\text{max}}} \log \left( \frac{I_0}{I} \right) d\tilde{\nu}
\]  \hspace{1cm} (A.5)

where \( I_0 \) is the intensity of the incident light, \( I \) the intensity of transmitted light, \( \sigma \) (cm\(^2\) mol\(^{-1}\)) the absorption cross section, \( l \) (cm) the optical path length, and \( \tilde{\nu}_0 \) (cm\(^{-1}\)) the frequency at maximum intensity of the absorption band.

172
The extinction in the FTIR program OPUS is determined by $\log_{10}$, however, the equation for the band strength is based on the Lambert-Beer law (Eq. A.1) using the natural logarithm. Therefore a conversion from $\log$ to $\ln$ needs to be included, which results in the multiplication with $\ln(10) = 2.303$.

The determined optical path length for the cooling cell in dependence of the number of passes is summarized in Table A.2 and visualized in Fig. A.1.

<table>
<thead>
<tr>
<th>No. of passes</th>
<th>total path length (cm)</th>
<th>path length (cm) / pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>284.1</td>
<td>71.1</td>
</tr>
<tr>
<td>8</td>
<td>431.4</td>
<td>54.0</td>
</tr>
<tr>
<td>12</td>
<td>567.7</td>
<td>47.3</td>
</tr>
<tr>
<td>16</td>
<td>723.4</td>
<td>45.2</td>
</tr>
<tr>
<td>20</td>
<td>826.8</td>
<td>41.3</td>
</tr>
<tr>
<td>24</td>
<td>944.6</td>
<td>39.4</td>
</tr>
<tr>
<td>28</td>
<td>1065.2</td>
<td>38.1</td>
</tr>
<tr>
<td>32</td>
<td>1193.6</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Figure A.1: Optical path length of the cooling cell depending on the number of passes.
### A.2 Measurement Settings FTIR

#### Table A.3: Spectrometer Bruker IFS 66v/S

<table>
<thead>
<tr>
<th>Variable</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>0.5 cm⁻¹</td>
</tr>
<tr>
<td>Beam splitter</td>
<td>KBr</td>
</tr>
<tr>
<td>Aperture</td>
<td>2 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>MCT</td>
</tr>
<tr>
<td>Mirror velocity</td>
<td>10; 80 kHz</td>
</tr>
<tr>
<td>Sample single gain</td>
<td>automatic</td>
</tr>
<tr>
<td>Background single gain</td>
<td>automatic</td>
</tr>
<tr>
<td>Delay after device change</td>
<td>2 s</td>
</tr>
<tr>
<td>Delay before measurement</td>
<td>0 s</td>
</tr>
<tr>
<td>Low pass filter</td>
<td>open</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>single sided fast return</td>
</tr>
<tr>
<td>Correlation mode</td>
<td>no</td>
</tr>
<tr>
<td>Phase resolution</td>
<td>8</td>
</tr>
<tr>
<td>Phase correction mode</td>
<td>Mertz</td>
</tr>
<tr>
<td>Apodization function</td>
<td>Norton-Beer, medium</td>
</tr>
<tr>
<td>Zerofilling factor</td>
<td>2</td>
</tr>
</tbody>
</table>

#### Table A.4: Spectrometer Bruker IFS 125HR

<table>
<thead>
<tr>
<th>Variable</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>0.5 cm⁻¹</td>
</tr>
<tr>
<td>Beam splitter</td>
<td>KBr</td>
</tr>
<tr>
<td>Aperture</td>
<td>5 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>MCT</td>
</tr>
<tr>
<td>Mirror velocity</td>
<td>80 kHz</td>
</tr>
<tr>
<td>Sample single gain</td>
<td>×1</td>
</tr>
<tr>
<td>Background single gain</td>
<td>×1</td>
</tr>
<tr>
<td>Delay after device change</td>
<td>0 s</td>
</tr>
<tr>
<td>Delay before measurement</td>
<td>0 s</td>
</tr>
<tr>
<td>Low pass filter</td>
<td>40 kHz</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>single sided, fast-forward</td>
</tr>
<tr>
<td>Correlation mode</td>
<td>off</td>
</tr>
<tr>
<td>Phase resolution</td>
<td>16</td>
</tr>
<tr>
<td>Phase correction mode</td>
<td>Mertz</td>
</tr>
<tr>
<td>Apodization function</td>
<td>Blackman-Harris 3-Form</td>
</tr>
<tr>
<td>Zerofilling factor</td>
<td>2</td>
</tr>
</tbody>
</table>
Appendix B

Determination of the Rate Constants $J_V$ and $J_S$

By recording IR spectra of the aerosols as a function of time during a phase transition at constant temperature, the volume and surface nucleation rate constants, $J_V(T)$ and $J_S(T)$, can be determined. A detailed discussion of the application of this approach to the homogenous freezing of supercooled droplets is provided in Sigurbjörnsson and Signorelli\textsuperscript{168}. The determination of the volume and surface freezing rate constants $J_V$ and $J_S$ for the freezing from an unfrozen state (phase A, e.g. supercooled) into a frozen state (phase B, e.g. crystalline) requires three major steps.

1. The determination of the fraction of particles $\bar{P}_{\text{exp}}(t)$ in the initial phase as a function of time from the experimental time dependent IR spectra.

2. The determination of the particle size distribution $f(x,t)$ as a function of time from the IR spectra using a Mie model.

3. A non-linear least squares fit of $\tilde{P}(t)$ (see Eq. B.2) to $\tilde{P}_{\text{exp}}(t)$ under consideration of the time-dependent particle size distribution.
B.1 Determination of $\bar{P}_{\text{exp}}(t)$

The experimentally determined average fraction $\bar{P}_{\text{exp}}(t)$ of particles in phase A is obtained by a linear decomposition of the IR spectra into their frozen and unfrozen components. First, the spectrum $S_0$ of the pure unfrozen phase A needs to be determined. This spectrum is usually the first spectrum recorded, immediately after sample injection and particle formation. For $S_0$, $\bar{P}_{\text{exp}}(t=0) = 1$, as all particles are assumed to be in phase A. $S_f(t_f)$ is the spectrum at time $t_f$ at which all particles are frozen (i.e. in phase B). For $S_f(t_f)$, $\bar{P}_{\text{exp}}(t = t_f) = 0$.

To determine $\bar{P}_{\text{exp}}(t)$ for a spectrum $S_i(t_i)$ with $0 < t_i < t_f$, $S_i$ and $S_f$ are scaled to the integral of the band that is used for decomposition of $S_0$. In the case of $n$-$C_5H_{12}$ and $n$-$C_4H_{10}$ the absorption band between 1420-1490 cm$^{-1}$ was used. Then, a combination spectrum $S_x(t_i)$ (Eq. B.1) of $S_0$ and $S_f$ is found to match the spectrum $S_i(t_i)$

$$S_x(t_i) = x \times S_0 + (1 - x) \times S_f \quad (B.1)$$

with $x = \bar{P}_{\text{exp}}(t)$. The determination of $S_x$ is done visually. Usually a range of values is found for $x$. The center of this range is chosen to be $x$. The deviation from $x$ forms the error range. An example for how well the decomposition works is illustrated in Fig. B.1. The dashed curve is vertically shifted by $\sim 3\%$ for better visualization.

![Figure B.1](image-url)

Figure B.1: The solid curve is the experimental spectrum, the dashed curve is the spectrum obtained from linear decomposition.
B.2 Determination of the Time-Dependent Particle Size Distribution

The rate constants $J_V$ and $J_S$ depend on the particle size. The particles size can be determined from experimental IR spectra. Elastic scattering of light by particles $> 100$ nm causes a slanted baseline in the IR spectrum as depicted in Fig. [B.2]. The extent of the slanted baseline depends on particle number concentration and particle size. Using a Mie model, the mean particle size $r(t)$ is estimated for a number of spectra between $t = 0$ and $t = t_f$. Using a Mie model a theoretical extinction spectrum can be calculated to match the experimental one. The model assumes a log-normal particle size distribution and requires a series of input parameters such as the complex refractive index. The full list of input parameters is provided in Table B.1. The input values of the particle number concentration $\times$ path length (particles/$\mu m^2$) and of the mean radius $r(t)$ ($\mu m$) are estimated from the concentration and density of the substance of interest in the cooling cell and under the current experimental conditions ($p, T$), respectively. The mean radius $r(t)$ is the input radius from the calculated spectrum that fits the experimental spectrum best. An example for an experimental and calculated spectrum as well as time evolution of $r(t)$ is shown in Fig. [B.2]. The Figure shows the lower and upper limit of calculated spectra (blue) that fit the experimental spectrum (red) best. For the spectrum shown ($\sim 100$ s after sample injection and particle formation) the mean particle radius is between 0.046 and 0.052 nm. $r(t)$ can be described by a polynomial function which is then used in the fit of $\bar{P}(t)$ to $\bar{P}_{exp}(t)$ to determine $J_V$ and $J_S$ (see Appendix B.3).

Table B.1: Data input for Mie model

<table>
<thead>
<tr>
<th>Geometric Standard deviation $\sigma$</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution</td>
<td>log-normal</td>
</tr>
<tr>
<td>Refractive index (medium)</td>
<td>1</td>
</tr>
<tr>
<td>Number of scattering angles</td>
<td>2</td>
</tr>
<tr>
<td>Number of grid points ($&lt; 100000$)</td>
<td>1000</td>
</tr>
<tr>
<td>Particle number concentration $\times$ path length (particles/$\mu m^2$)</td>
<td></td>
</tr>
<tr>
<td>Mean radius ($\mu m$)</td>
<td></td>
</tr>
</tbody>
</table>
Figure B.2: Calculated (blue) and experimental (red) spectra of n-C₅H₁₂ at 78 K at ~ 100 s after sample injection and particle formation and the time-dependent mean particle size r(t) (insert). The calculated spectra represent the lower and upper limit for the mean particle radius, 0.046 and 0.052 nm, respectively. The intensity of the slanted baseline depends on the particle size and the particle number concentration.

B.3 Non-linear Fit to Determine Jᵥ and Jₛ

The experimental data of $\bar{P}_{exp}(t)$ is fitted by a non-linear least square fit. The fit considers the change of particle size over time using the polynomial function of r(t) determined in the previous section, and optimizes $J_V$ (with $J_S = 0$) and $J_S$ (with $J_V = 0$) for Eq. [B.2]

$$\bar{P}(t) = \int \frac{f(x,t)V(x)e^{-[J_V(T)V(x)+J_S(T)S(x)]]t}dx}{\int f(x,t)V(x)dx}$$  \hspace{1cm} (B.2)

where $\bar{P}(t)$ is the average volume fraction of particles at time t that are still in the initial phase (phase A). $f(x,t)$ denotes the particle size distribution of the particle ensemble, where $x = \ln(r/u)$ is the logarithm of the particle radius r in units of $u = 1$ nm. $V(x)$ and $S(x)$ are the particle volume and the particle surface area, respectively. Eq. [B.2] considers both volume and surface contributions to nucleation, one of which usually dominates.\(^{[168]}\)
Appendix C

Sensitivity Analysis for the Determination of the Rate Constant $J$

The uncertainty of the volume and surface rate constants $J_V$ and $J_S$, respectively, depends on the variation of several variables. Most of these variables affect the particles size distribution and the probability $\bar{P}_{\text{exp}}(t)$ to find the fraction of particles in the initial phase, phase A.

The particle size distribution is affected by

- the complex refractive index data
- the geometric standard deviation
- the integration band for scaling

$\bar{P}_{\text{exp}}(t)$ is affected by

- the spectrum of the initial phase A, $S_0(t = 0)$, and spectrum of the crystallized phase B, $S_f(t = t_f)$, used for decomposition
- the integration band for scaling

A sensitivity analysis was performed for both, $n$-C$_4$H$_{10}$ and $n$-C$_5$H$_{12}$, to determine how the variation of the above variables affects $J_V$ and $J_S$. Here, the analysis for $n$-C$_4$H$_{10}$ is presented. In both cases, $n$-C$_4$H$_{10}$ and $n$-C$_5$H$_{12}$, the analysis shows that the effect on the rate constants lies within one order of a magnitude.
C.1 Particle Size Distribution

C.1.1 Complex Refractive Index Data

Wavelength dependent complex refractive index data for \( n-C_4H_{10} \) in the IR region are not available. However, the complex refractive index is needed to determine the particle size from experimental spectra using Mie scattering. The particle size distribution was determined using the complex refractive index data of liquid \( n-C_5H_{12} \) and solid CO\(_2\).\(^{214,219}\) As a result, the mean radius \( r(t) \) of the \( n-C_4H_{10} \) particles is larger when the refractive index data of CO\(_2\) is used compared to the refractive index data of \( n-C_5H_{12} \). The effect on the rate constants \( J_V \) and \( J_S \) for the second phase transition of \( n-C_4H_{10} \) aerosol particles is within one order of magnitude as shown in Table C.1

Table C.1: Comparison of the rate constants \( J_V \) and \( J_S \) determined using the refractive index data of solid CO\(_2\) and liquid \( n-C_5H_{12} \)

<table>
<thead>
<tr>
<th></th>
<th>CO(_2)</th>
<th>( n-C_5H_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_V \ \text{cm}^{-3} \text{s}^{-1} )</td>
<td>( 2 \times 10^{12} )</td>
<td>( 1 \times 10^{11} )</td>
</tr>
<tr>
<td>( J_S \ \text{cm}^{-2} \text{s}^{-1} )</td>
<td>( 7 \times 10^{13} )</td>
<td>( 5 \times 10^{12} )</td>
</tr>
</tbody>
</table>

C.1.2 Integration Band for Scaling

A specific IR \( n-C_5H_{12} \) band of the calculated spectrum is scaled so that the mole fraction of the calculated \( n-C_5H_{12} \) spectrum equals the mole fraction of the experimental \( n-C_4H_{10} \) IR spectrum. Therefore, several experimental IR spectra of \( n-C_5H_{12} \) and \( n-C_4H_{10} \) at the same concentration were recorded to determine the ratio of the intensities of specific bands. The ratios for two bands were determined. The first integration range was from 1490-1420 cm\(^{-1}\) for \( n-C_5H_{12} \) and \( n-C_4H_{10} \), and the second range was from 740-725 cm\(^{-1}\) for \( n-C_5H_{12} \) and 740-720 cm\(^{-1}\) for \( n-C_4H_{10} \). This result in a ratio of \( n-C_5H_{12}:n-C_4H_{10} = 1.113 \) and 1.283, respectively.

In theory both ratios can be used and both ratios should lead to the same scaled spectrum. However, this is only true for the experimental spectra, but not for the calculated one that is used to determine the particle size. The reason is, that the calculated spectrum uses the complex refractive index data of liquid \( n-C_5H_{12} \) at room temperature whereas experimental
spectra were recorded at 78 K. The ratio of I(1490-1420 cm\(^{-1}\)):I(740-725 cm\(^{-1}\)) is different at 78 K compared to 293 K. This results in a different scaled spectrum and therefore in a different particle size depending on which band was used for scaling. Particles were larger when I(1490-1420 cm\(^{-1}\)) was used for scaling. The effect on the values for \(J_V\) and \(J_S\) for the second phase transition of \(n\)-C\(_4\)H\(_{10}\) aerosol particles is shown in Table C.2. The error lies within one order of magnitude.

Table C.2: Comparison of the rate constants \(J_V\) and \(J_S\) determined using the absorption bands at 740-720 cm\(^{-1}\) and 1490-1420 cm\(^{-1}\) for scaling and integration

<table>
<thead>
<tr>
<th></th>
<th>720-740 cm(^{-1})</th>
<th>1420-1490 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J_V) cm(^{3})s(^{-1})</td>
<td>5\times10(^{11})</td>
<td>1\times10(^{11})</td>
</tr>
<tr>
<td>(J_S) cm(^{2})s(^{-1})</td>
<td>1\times10(^{13})</td>
<td>5\times10(^{12})</td>
</tr>
</tbody>
</table>

C.1.3 Geometric Standard Deviation \(\sigma\)

For the determination of the particle size distribution a log-normal distribution of the particle sizes with mean particle radii \(r(t)\) and a time independent geometric standard deviations \(\sigma\) are assumed.\(^{[4][17][218]}\) \(r(t)\) and \(\sigma\) are strongly correlated and Mie fits only allow to determine one of them independently.\(^{[218]}\) \(\sigma\) is set to 1.6, which is a typical value for aerosol particles formed in cooling cells. However, to estimate the uncertainty in the rate constants \(J_V\) and \(J_S\) caused by the variation of \(\sigma\) the particle size distribution was also determined for \(\sigma = 1.2\) and 2.0. The variation in \(\sigma\) affects the mean particle radius \(r(t)\): \(r(t)(\sigma = 1.2) > r(t)(\sigma = 1.6) > r(t)(\sigma = 2)\). The uncertainty of the rate constants \(J_V\) and \(J_S\) caused by the variation of \(\sigma\) and therefore by the change in particle size is within one order of magnitude, as summarized in Table C.3.

Table C.3: Comparison of the rate constants \(J_V\) and \(J_S\) determined using a geometric standard deviation of \(\sigma = 1.2\), 1.6, or 2.0

<table>
<thead>
<tr>
<th></th>
<th>(\sigma = 1.2)</th>
<th>(\sigma = 1.6)</th>
<th>(\sigma = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J_V) cm(^{3})s(^{-1})</td>
<td>7\times10(^{12})</td>
<td>4\times10(^{12})</td>
<td>2\times10(^{11})</td>
</tr>
<tr>
<td>(J_S) cm(^{2})s(^{-1})</td>
<td>7\times10(^{11})</td>
<td>2\times10(^{12})</td>
<td>6\times10(^{12})</td>
</tr>
</tbody>
</table>
C.2 \( \bar{P}_{exp}(t) \)

\( \bar{P}_{exp}(t) \) is obtained from a linear decomposition of the IR spectra into their frozen and unfrozen components. This involves two steps: (i) the uncrystallized and crystallized spectrum needs to be found \( (S_0(t = 0) \text{ and } S_f(t = t_f)) \), respectively), and (ii) scaling the band used for decomposition (either 740-720 or 1490-1420 cm\(^{-1}\)) to the integral of the band of the uncrystallized spectrum (phase A). The scaling is necessary since the IR signal decreases over time due to diffusion of particles out of the IR beam. In both cases, the effect on \( \bar{P}_{exp}(t) \) is small and results in an uncertainty for the rate constants \( J_V \) and \( J_S \) within an order of one magnitude.