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ANAS AL NATSHEH

Quantum Mechanics Study of Molecular Clusters Composed of Atmospheric Nucleation Precursors

Doctoral dissertation

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ABSTRACT

Atmospheric particles influence the Earth's climate by affecting cloud properties and the levels of precipitation. New particle formation, which is frequently observed in the lower troposphere and stratosphere, is an important source of atmospheric aerosols. A clear understanding of particle formation mechanisms is essential if one wishes to make a quantitative assessment of the climate-related health and the environmental impacts of atmospheric aerosols. However, mechanisms of particle formation in the atmosphere have remained elusive despite decades of intensive research.

In the first part of this thesis, the electrical properties (dipole moment) of the molecular clusters of mono, di and trihydrates of sulfuric acid have been investigated using quantum mechanics. A method based on Density Functional Theory (DFT) has been applied. Generally, we found that hydrated sulfates are highly polar compounds. The present results also show that clusters of a similar chemical composition may exhibit a very large difference in their dipole moments. These variations lead to significant variations (up to 230%) in the uptake of sulfuric acid by the ionic clusters.

The second part of this thesis is devoted to the origin of sign preference phenomena, which has been studied by using quantum mechanics. It has been found that the sign preference phenomenon, which has remained puzzling for more than a century, is essentially quantum in nature. It is demonstrated that the effect of the chemical identity of the core ion is controlled by the electronic structure of the core ion through the influence on the intermolecular bonding energies during the initial steps of cluster formation.

In the last part of the thesis, the mono-, di- and trihydrates of nitric acid have been studied and their thermodynamics properties have been calculated. Di- and trihydrates of nitric acid are the dominating composition of crystals in the polar stratospheric clouds. The heterogeneous chemical reactions, which occur on the surface of these crystals lead to the activation of chlorine atoms and this can result in ozone depletion. In this study, two new molecular structures of nitric acid dihydrates and one new modification of nitric acid trihydrates have been identified. Formation pathways for all the di- and trihydrates of the nitric acid have been investigated using the thermodynamical properties. This study leads to the conclusion that nitric acid is present in the polar stratospheric clouds crystals in the form of a phase mixture, and it is composed of the most stable isomers of di- and trihydrates of nitric acid (β-NAT and β-NAD).

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CAB Thesaurus: atmosphere; aerosols; particles; nucleation; sulfuric acid; sulfates; nitric acid; precursors; clusters; hydration; thermodynamics; chemical structure; electrical properties; clouds; polar regions; crystals; chlorine; ozone depletion; climate; environmental impact

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Kuopio, May 2006

Anas Al Natsheh
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ABBREVIATIONS

BHN:	Binary homogenous nucleation
CC:	Coupled cluster
CI:	Configuration interaction
CID:	Configuration interaction for doubly excited determinants
CISD:	Configuration interaction for singly and doubly excited determinants
DFT:	Density functional theory
DNT:	Dynamic nucleation theory
GEA:	Gradient expansion approximation
GGA:	Generalized gradient approximation
HF:	Hartree-Fock method
IIN:	Ion induced nucleation (Thomson theory)
IMN:	Ion-mediated nucleation
LDA:	Local density approximation
LSDA:	Local spin density approximation
MC:	Monte Carlo simulation
MP*n*:	*n*th-order Møller-Plesset (perturbation theory)
NAD:	Nitric acid dihydrates
NAM:	Nitric acid monohydrates
NAT:	Nitric acid trihydrates
PPM:	Parts per million
PSC:	Polar stratospheric clouds
QM:	Quantum mechanics
RH:	Relative humidity
THN:	Ternary homogenous nucleation

LIST OF ORIGINAL PUBLICATIONS

The thesis consists of an introductory section followed by five articles. The published articles are reproduced with the kind permission of the publishers.

Paper I	A. Al Natsheh, A. B. Nadykto, K.V. Mikkelsen, F. Yu and J. Ruuskanen Sulfuric acid and sulfuric acid hydrates in gas phase: A DFT investigation Journal of Physical Chemistry A, 108(41), p 8914-8929, 2004
Paper II	A.B. Nadykto, A. Al Natsheh, F. Yu, K.V. Mikkelsen, and J. Ruuskanen Effect of molecular structure and hydration on the uptake of gas-phase sulfuric acid by charged ultrafine particles/clusters Aerosol Science and Technology, 38(4), p 349-353, 2004
Paper III	A.B. Nadykto, A. Al Natsheh, F. Yu, K.V. Mikkelsen, and J. Ruuskanen Quantum nature of the sign preference in the ion-induced nucleation Physical Review Letters, 96(12), Art.No.125701, 2006
Paper IV	A. Al Natsheh, K.V. Mikkelsen, J. Ruuskanen Theoretical investigation of the coexistence of α and β-nitric acid trihydrates (NAT) molecular conformations Chemical Physics, 324(1), p 210-215, 2006
Paper V	A. Al Natsheh, A. B. Nadykto, K.V. Mikkelsen, F. Yu and J. Ruuskanen Coexistence of metastable nitric acid dihydrates: A molecular level contribution to understanding the polar stratospheric clouds formation Chemical Physics Letters, In press, 2006

CONTENTS

1 INTRODUCTION

Knowledge about the physical and chemical properties of molecules and clusters from which liquid and solid aerosol particles are built, is necessary if one is to obtain a clear understanding of aerosol formation mechanisms and to be able to make an accurate assessment of the impact of atmospheric aerosols on the climate forcing.

Aerosols, which are composed of small particles suspended in a gaseous mixture, affect the radiation balance in the atmosphere by scattering and absorbing solar and infrared radiation. Aerosols influence the cloud formation through the size and number concentrations of droplets and ice particles which then results in changes in the cloud properties

The importance of understanding the very early stage of cluster formation arises from the fact that the particle nucleation rates are very sensitive to the thermodynamics of the initial steps of the cluster growth. Understanding the initial growth steps is critical for a number of processes related to atmospheric modelling, industry, and assessment of the public health effect of ultrafine particles.

Water, sulfuric and nitric acids and possibly ammonia are the key substances involved in the atmospheric aerosol formation. Although water molecules dominate in the composition of condensable vapors in the atmosphere, water alone cannot nucleate under typical atmospheric conditions where relative humidity (RH) < 100 %. The presence of the sulfuric acid and other precursors, which have very low vapour pressures helps water molecules to participate in this process. In addition, short-range molecular properties such as dipole moment and electric charge facilitate cluster formation. Since they are both dipolar in character, water and sulfuric acid strongly interact with ions. The presence of ions, which essentially function as a catalyst, helps to overcome the nucleation barrier and may lead to a significant enhancement of nucleation rates. Nucleation on ions is one of the important nucleation mechanisms in the Earth's atmosphere and it may play an essential role in a number of climate-related processes. Unfortunately, despite decades of intensive research, actual nucleation mechanisms remain poorly understood and this a source of major uncertainty (Houghton and Intergovernmental Panel on Climate Change Working Group, 2001).

Strong interactions between ionic clusters and dipolar atmospheric precursors, common pollutants, toxic, hazardous and chemically-active substances promote the formation of ultrafine aerosol particles that are associated directly with adverse public health effects. Public health studies have shown that sulfuric acid in an aerosol form may cause a serious health problems such as lung cancer and irritation to the upper respiratory tract (Brimblecombe and Maynard, 2001; Soskolne et al, 1989). On the other hand, the main health effects of nitrogen compounds appear to be due to NO which can become attached to the blood hemoglobin and reduce the efficiency of the oxygen transport. Severe exposure to NO_2 can be very harmful with symptoms varying from inflammation of lung tissues to death in severe cases (Manahan, 2000).

Sulfuric acid is likely hydrated in the atmosphere and, thus, in order to estimate the uptake of the sulfuric acid by ionized clusters in the atmosphere, the electrical dipole moments of the hydrates that are involved in the dipole-charged interaction with the ionic clusters have to be calculated.

Nucleation experiments have shown that in a variety of systems, the nucleation rates of positive and negative ions may be different. Wilson's pioneering cloud chamber experiments (Wilson, 1897) demonstrated that ions of opposite sign exhibited significantly different nucleation rates. This phenomenon is known as the sign preference but it has remained a mystery for more than a century. Despite impressive progress in the experimental techniques since Wilson's original work, precise nucleation measurements remain difficult due to uncertainties in their interpretation and even today some experimental results are still controversial.

The critical importance of the chemical identity of the core ion was established by Castleman and Tang (Castleman and Tang, 1972), who noted that ‘‘understanding the effect of ions would be very difficult, or even impossible; if the ion's specific chemical characteristics had a significant effect on their nucleating efficiency”.

To resolve the fundamental problem of the sign preference, it is necessary to address the following questions: a) What are the mechanisms and the key parameters controlling the sign preference? b) At which stage does the sign preference have a large effect on the cluster formation and growth? and c) Which theory or theories can account properly for the chemical identity of the core ion, and could be used, with a sufficient degree of confidence, for interpreting nucleation experiments and designing nucleation thermodynamic models?

While sulfuric acid and water play a key role in the Earth troposphere, nitric acid (NA), which is present in the stratosphere in the form of mono- (NAM), di-(NAD), and tri-(NAT) hydrates of nitric acid largely control the formation and the properties of polar stratospheric clouds (PSCs). NAD and NAT are the main components of PSCs ice crystals and liquid that lay the foundation for chlorine activation and subsequent ozone depletion.

NAT are usually considered dominating in the composition of certain types of PSCs due to their thermodynamic stability. However, it has been suggested that under the stratospheric conditions, the formation of hydrates, which are less stable and differ from NAT in their catalytic and optical properties as well as solubility of HCl, is also possible (Arnold, 1992). Worsnop et al. have proposed that under the stratospheric conditions, the formation of metastable NAD may be favorable due to the lower potential barrier for NAD formation compared to that of NAT formation (Worsnop et al, 1993).
Although the importance of a clear understanding of the formation mechanisms and thermodynamics of hydrates of nitric acid in the stratospheric conditions has been long established, the detailed formation pathways for different NAD and NAT molecular structures, as well as NAD→NAT and NAT→NAT transformations and NAT stability still remain unclear. Another important factor that obscures the picture is that recent spectroscopic studies have indicated the presence of a second NAD and NAT molecular conformations not predicted by existing theoretical studies (Grothe et al, 2004; Koehler et al, 1992; Tizek et al, 2004). Currently, no information is available about the chemical and physical properties of these molecular structures. This formed the impetus for a theoretical investigation of properties, formation and transformation mechanisms for nitric acid hydrates under stratospheric conditions.

The present thesis examines the structure and properties of clusters composed of the atmospheric precursors. The structure and properties of water and binary sulfuric acid-water and nitric acid-water clusters have been investigated using Density Functional Theory (DFT). Structures and polarities of mono-, di- and tri-hydrates of the sulfuric acid have been investigated in the present thesis using quantum theory at the DFT level. It has been found that the vast majority of hydrates studied are highly dipolar and this leads to a significant (over 130%) enhancement of the uptake of the sulfuric acid under atmospheric conditions.

In the present thesis the formation of molecular clusters around core ions of different signs and chemical compositions has been investigated using quantum theory. It has been found that the chemical identity of the core ions has a substantial effect on the properties of clusters formed around the core ions. It has been demonstrated that the sign preference is essentially quantum in nature and controlled by the electronic structure of the core ion through the influence on the intermolecular bonding energies during the initial steps of cluster formation. The present study reveals the decisive role of the initial stages of the ion clustering in the formation of the sign preference, and highlights serious deficiencies in the existing ion-induced nucleation theories, in which the electronic structure of the core ion has either been ignored or has not been treated rigorously. Our contributions demonstrate that a quantum theory that treats the cluster in a rigorous manner provides a solid foundation for the development of a new first-principle ion-induced nucleation theory.

In the present thesis, the structures and properties of hydrated nitric acid have been studied using DFT. Three equilibrium conformers of NAD (α, β and γ- NAD) and two molecular structures of NAT (α, β-NAT) have been identified and described. The thermochemistry of α-, β-NAD, α-, β-NAT and NA→NAM→NAD→NAT transformations has been investigated and the thermodynamic stability of NAT is discussed. We found that the difference in the formation free energy between α-NAD and β-NAD, as well as the difference between α-NAT and β-NAT was very small. A comparison of the thermodynamic data for α and β-NAD and α and β-NAT revealed that the formation of NAT from NAD is favorable thermodynamically only if α-NAD→α-NAT transformation at a temperature T<195 K occurs. Formation of NAT from the nitric acid or NAM is generally more favorable thermodynamically than NAD → NAT transformation; however, the direct nitric acid-NAT and NAM→NAT processes under the stratospheric conditions are limited kinetically. The small difference in the formation free energies of NAM, α-NAD, β-NAD, α-NAT and β-NAT suggests that hydrated nitric acid in the Earth stratosphere is not unimolecular and it will be present in PSC in the form of (NAM)-(α-NAD)-(β-NAD)-(α-NAT) and β-NAT phase mixtures. However, thermodynamic arguments are not the only factors governing the formation and evolution of nitric acid hydrates. Other important factors include the strong hygroscopic nature of nitric acid and the availability of water molecules. Based on the kinetic estimations, we predict that the final phase mixture is composed of β-NAD and β-NAT.

2 BACKGROUND

This chapter gives an overview of the main aspects and basic principles relevant to the present thesis, including the fundamentals of the aerosol formation processes and modeling, the microphysics of sulfuric and nitric acids and their hydrates and the thermochemistry of the ozone depletion under stratospheric conditions.

2.1 Particulate matter: an overview

Particulate matter or *Aerosol* is defined as a suspension of solid or liquid particles in a gas (Hinds, 1999; Seinfeld and Pandis, 1997). The existence of aerosol particles in the atmosphere is a natural phenomena and it can be caused by different sources e.g. volcanoes, dust, sea spray and anthropogenic activities (Seinfeld and Pandis, 1997). The size of the aerosol particles can vary widely from a few nano-meters to tens or even hundreds of micro-meters. Generally, aerosol particles can divided into two distinct categories: *primary aerosols* particles which are emitted directly from a source (e.g dust) and the *secondary aerosols* particles, which are formed through the gas-to-particle transition in the atmosphere (e.g. fog) (Seinfeld and Pandis, 1997). The lifetime of aerosol particles in the atmosphere can vary from a few seconds to a few years this being dependent on their chemical composition and the surrounding environment.

2.1.1 Aerosols formation/ nucleation

Nucleation processes play a fundamental role in natural and industrial processes. Natural nucleation is one of the key processes controlling the aerosol particle formation in the Earth's atmosphere, including aerosol particle formation related to global warming processes e.g. (Kulmala, 2003), the effect of cosmic rays e.g. (Yu and Turco, 2000) and the formation of Polar Stratospheric Clouds (PSCs) e.g. (Seinfeld and Pandis, 1997), while controlled nucleation is utilized in various industrial processes such as preparation of the glass ceramics for the biomedical, automotive and aerospace applications, synthesis of nanocrystalline materials, phase-change-optical-recording, protein crystallization and cryo-preservation (Granasy and James, 1999).

An accurate theoretical description of the nucleation processes is important, as the models used to simulate the atmospheric aerosol formation are very sensitive to the nucleation rates see e.g. (Kulmala, 2003; Nadykto and Yu, 2004b). Nucleation in the atmosphere has been intensively studied during the last century; however, there are still uncertainties concerning how nucleation occurs in the atmosphere and the principal nucleation mechanism or mechanisms of the atmospheric nucleation are still a mystery (Houghton and Intergovernmental Panel on Climate Change Working Group, 2001). Presently, there are three main candidate theories to account for atmospheric nucleation: binary homogeneous nucleation of sulfuric acid and water (BHN), ternary homogeneous nucleation (THN) involving ammonia in addition to sulfuric acid and water and ion-mediated nucleation (IMN).

While homogeneous nucleation has been considered as a potential nucleation mechanism for decades, the nucleation of atmospheric ions was considered to be negligible for a long time until the publication Yu and Turco (Yu and Turco, 2001), who performed direct kinetic simulations of ion nucleation and pointed out that the nucleation of atmospheric ion is much stronger than was assumed earlier. The earlier conclusion about the negligible contribution of ions to the atmospheric nucleation was based on the classical Thomson theory (IIN), which predicted a very small ion effect on the nucleation rates and no ion-induced nucleation in the atmospheric conditions. The insufficient predictivity of IIN has been long known; however, recent experimental studies have shown that IIN fails to describe the properties of small ionic clusters and it is incapable of explaining the pronounced charge effect observed in the nucleating polar vapours. The fundamental problems of IIN were routinely attributed in the literature to limited validity of the capillarity approximation and liquid droplet model formalism and they remained unsolved until Nadykto and Yu (Nadykto and Yu, 2004a; Nadykto and Yu, 2003) suggested that these problems arise mainly from neglecting the electrostatic interactions between charged cluster and polar vapor monomers in the gas phase.

In a series of recent publications (Nadykto et al, 2003; Nadykto and Yu, 2004a; Nadykto and Yu, 2003; Nadykto and Yu, 2004b) it has been have pointed out that the dipole moment of condensing molecules and molecular pre-critical clusters is a novel and fundamental parameter controlling ion nucleation and the classical IIN theory has been corrected accordingly (Nadykto and Yu, 2004b). The net effect of taking into account the dipole-charge interaction on the ion-induced nucleation has been a substantial enhancement of the nucleation rates. The electrostatic interactions of polar vapor monomers and small molecular clusters with charged ion core are responsible for both the enhancement of the uptake/condensation coefficient (Nadykto and Yu, 2003) and reduction of the evaporation (Nadykto et al, 2003; Nadykto and Yu, 2004a; Nadykto and Yu, 2004b). The revised classical IIN theory (Nadykto and Yu, 2004b) with the dipole-charge interaction incorporated has a substantially improved predictivity and this not only accounts for the discrepancies between the classical IIN theory and the experimental data but also accurately predicts the pronounced charge effect on the nucleation rates in polar vapors observed in several experiments. The large systematic deviation of the conventional Millikan-Fuchs mobility equivalent diameter obtained from the experimental data on ion mobility no longer differs from the theoretical Kelvin-Thomson diameter (Nadykto et al, 2003) when the Kelvin-Thomson equation is corrected by the dipole-charge interaction. However, despite significant progress in correcting the classical theory, the dependence of the nucleation rates on the chemical nature of the core ion in the classical theory is still unknown and the origin of the fundamental phenomenon of the sign preference has remained unclear up until now.

2.2 Sulfuric acid and its hydrates

The relatively low concentration of sulfur in the Earth's crust and atmosphere, (500 and 1 ppm, respectively), has not prevented it from being of one of the most important participants in the chemistry of the atmosphere (Seinfeld and Pandis, 1997). Sulfur is present in different compounds e.g. dimethyl sulfide, sulfuric acid, sulfur dioxide and sulfate and bisulfate ions (Seinfeld and Pandis, 1997).

Sulfur is emitted to the atmosphere as either hydrogen sulfide (H_2S) or sulfur dioxide (SO_2). Both gases are toxic and considered as primary air pollutants. The oxidation of the H_2S

through the reaction with the hydroxyl radical leads to the formation of SO_2 and the subsequent formation of the sulfuric acid and sulfate salts (Manahan, 2000). The nature of these reactions in the atmosphere is very complex due to the large number of factors such as temperature, humidity, light intensity, atmospheric transport and surface characteristics of particulate matter (Manahan, 2000) that can affect the reaction rates.

Sulfuric acid is highly hygroscopic because it is a dehydrated substance and it has two protons, which dissociate in two steps (Re et al, 1999). The ability of the sulfuric acid to absorb water even at very low humidity makes this substance extremely important for atmospheric nucleation (Berndt et al, 2005; Seinfeld and Pandis, 1997).

2.3 Nitrogen compounds in the atmosphere

Nitrogen dominates the composition of the Earth's atmosphere. Approximately 78% of the atmosphere volume is elemental nitrogen (Manahan, 2000). N_2 which is the main nitrogen compound in the atmosphere is very stable. N_2 that can break down through organic and inorganic chemical reactions is considered to be a limiting factor in the nitrogen cycle (Manahan, 2000). Other nitrogen compounds in the atmosphere include N_2O, which is next to N_2 in importance, and there are also traces of HNO_3, NO_2, NO, and NH_4NO_3.

Nitric acid is (HNO_3) is one of the most important substances in the atmosphere and its presence directly influences ozone depletion in the stratosphere. During the daytime nitric acid formation occurs mainly due to the reaction of nitrogen dioxide (NO_2) with the hydroxyl radical ($OH^{\cdot}$) however at night, the reaction path for the HNO_3 formation may be different (Seinfeld and Pandis, 1997). The oxidation of nitric dioxide leads to the formation of the nitrate radical ($NO_3^{\cdot}$) and this is followed by the production of dinitrogen pentoxide (N_2O_5), which reacts with water to form nitric acid (Seinfeld and Pandis, 1997).

2.3.1 Polar stratospheric clouds (PSCs)

The very low temperature (~183K) and long night in the polar regions provides the possibility for the very small amount of water present at 15-20km heights to condense and form polar stratospheric clouds (PSCs) (Seinfeld and Pandis, 1997).

There are two types of PSCs: PSC I and PSC II. PSCs of type I can be further sub-divided into two distinct categories: Ia and Ib. Non-spherical crystals of Ia consists mainly of nitric acid hydrates that are expected to be present in the form of nitric acid trihydrates (NAT). An insignificant amount of the sulfuric acid could also be present in PSCs of this type (Seinfeld and Pandis, 1997). The Ib type consists of a $HNO_3/H_2SO_4/H_2O$ gaseous mixture that leads to the formation of ternary supercooled liquid droplets (Seinfeld and Pandis, 1997; Tizek et al, 2004).The second type of the PSCs, the type II, is typically composed of non-spherical water ice crystals (Seinfeld and Pandis, 1997; Tizek et al, 2004).

2.3.1.1 PSCs and ozone depletion

Due to the essential role of PSCs in chlorine activation and subsequent ozone depletion, the physical chemistry of PSCs has been investigated intensively during recent decades. This section contains a brief description of the chemical reactions associated with the ozone depletion under stratospheric conditions.

The key reactions governing the ozone depletion are

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (2.3.1)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (2.3.2)$$

Catalytic reactions (2.3.3) and (2.3.2) continue until they are terminated by one of the following reactions

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (2.3.4)$$

$$Cl + CH_4 \rightarrow HCl + CH_3, \qquad (2.3.5)$$

which convert the atomic chlorine into a photo-chemically inert species that does not react with ozone (Zondlo et al, 2000). Here M is an arbitrary deactivating molecule.

The above reactions would be dominating, if the chemistry were to be limited to the gas phase only. However, the surfaces of PSCs particles act as a site for heterogeneous chemical reactions, leading to the re-activation of chlorine (Solomon et al, 1993; Zondlo et al, 2000). Three main reactions occurring on the PSCs surfaces can renew the sources of the active form of chlorine.

$$ClONO_2 + HCl \xrightarrow[\text{surfaces}]{\text{PSCs}} Cl_2 + HNO_3 \qquad (2.3.6)$$

$$HCl + HOCl \xrightarrow[\text{surfaces}]{\text{PSCs}} Cl_2 + H_2O \qquad (2.3.7)$$

$$Cl_2 \xrightarrow{hv} 2Cl \qquad (2.3.8)$$

Since the concentration of atomic oxygen in PSCs is low, the possibility for reactions (2.3.1) and (2.3.2) to continue is limited and the productivity of these reactions is insufficient to deplete the ozone layer in the stratosphere (Zondlo et al, 2000). Instead, the following reactions take place

$$2 \times (Cl + O_3 \rightarrow ClO + O_2) \qquad (2.3.9)$$

$$ClO + ClO + M \rightarrow (ClO)_2 + M \qquad (2.3.10)$$

$$(ClO)_2 + h\upsilon \rightarrow ClO_2 + Cl \qquad (2.3.11)$$

$$ClO_2 + M \rightarrow Cl + O_2 + M \qquad (2.3.12)$$

The reactions (2.3.8-11) continue unabated until the exhaustion of the chlorine inert species ($ClONO_2$ and HCl) which are produced through reactions (2.3.3) and (2.3.4).

Several other reactions take place on the PSCs surface. The denitrification process, which is one of these reactions, is expected to occur through the following reactions steps:

$$ClONO_2 + H_2O \xrightarrow[\text{surfaces}]{\text{PSCs}} HOCl + HNO_3 \qquad (2.3.13)$$

$$N_2O_5 + H_2O \xrightarrow[\text{surfaces}]{\text{PSCs}} 2\ HNO_3 \qquad (2.3.14)$$

$$HNO_3\ (\text{gas}) \xrightarrow[\text{surfaces}]{\text{PSCs}} HNO_3\ (\text{adsorbed}) \qquad (2.3.15)$$

These reactions lead to the formation of the condensed phase of nitric acid and the removal of the NO_2 sources from the gas phase. This leads to a reduction in the amount of nitrogen dioxide needed to deactivate chlorine monoxide to $ClONO_2$ (Zondlo et al, 2000).

The next step after the formation of nitric acid is the hydration of nitric acid. This process will be discussed in detail in the next section.

2.3.2 Nitric acid hydrates under stratospheric conditions

The importance of gas-phase mono-, di-, and tri-hydrates of nitric acid is related to their role in the formations of crystals/ solid particles that actively participate in the heterogeneous chemistry of chlorine activation and ozone depletion.

Nitric acid dihydrates (NAD) and trihydrates (NAT) are considered to be the building blocks of the PSCs type Ib crystals and, thus, it is critical to understand accurately the formation/

nucleation, transformation and growth processes of the NAD and NAT is critically important. Figure 2.1 shows possible formation pathway of α-NAT.

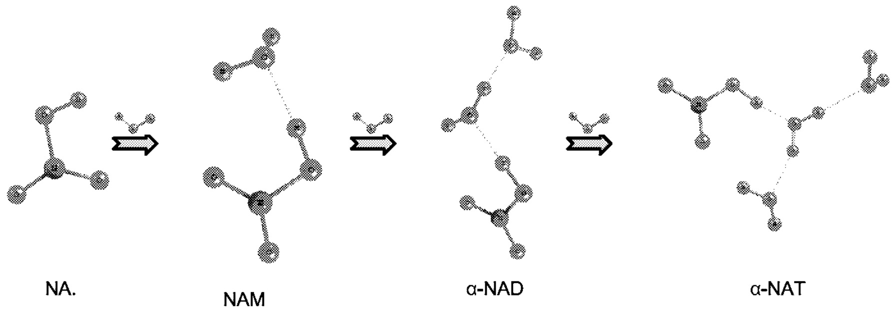


Figure 2.1 Possible formation pathway of α-NAT

Zondlo et al (Zondlo et al, 2000) have presented the possible formation scenarios of the NAD and NAT under stratospheric conditions:

1. Homogenous nucleation of the NAD and NAT from a ternary ($H_2SO_4/HNO_3/H_2O$) supercooled liquid. However, the experimental study by Koop et al. (Koop et al, 1997) revealed that the presence of H_2SO_4 could prevent the NAT formation. The experiments of Prenni et al (Prenni et al, 1998) indicated that the formation of NAT from the binary solution takes several hours while NAD formation occurs much quicker (Bertram and Sloan, 1998; Prenni et al, 1998).

2. The second scenario occurs regardless of whether the ice-liquid-gas phases equilibrium is maintained throughout the formation process or not. In the case when the equilibrium is reached, the growth rate of the ice core should be slower than the uptake rate of water molecules from the gas-phase by the liquid surface. These conditions allow the ice core to grow to its equilibrium size with the binary HNO_3/H_2O supercooled liquid volume and to become equal to the pre-existed aerosol particle volume. In the second case, no equilibrium exists between the ice core and the liquid and this leads to the fast growth of the ice germ by freezing the surrounding

water molecules and consequently, increasing the concentration of the nitric acid. These conditions could permit the homogenous nucleation of NAD or NAT (Bertram and Sloan, 1998; Prenni et al, 1998). The third possibility is a heterogeneous nucleation of NAD or NAT onto the ice core that occurs regardless of the equilibrium state between the solid-liquid-gas phases. This mechanism leads to the formation of mixed crystals composed of NAD, NAT and ice.

3. The third scenario can be described as the formation of an amorphous solid solution consisting of water, nitric and a few sulfuric acid molecules without any hydrate formation. This scenario requires a temperature of about 155 K, which is well below the ambient temperature in the typical stratospheric condition. This makes the formation probability for such structures very low, if not negligible.

On the other hand, field observations in the Arctic show a widespread occurrence of Ia type of PSCs. These observations point to the possibility for the formation of NAD and NAT crystals without the need for an ice surface. Unfortunately, currently no clear scenario exists to account for this formation mechanism (Zondlo et al, 2000).

3 QUANTUM COMPUTATIONAL METHODS

This chapter presents a review of different quantum computation methods and details of Density Functional Theory (DFT) methods used in this thesis.

3.1 Overview

The structure and thermodynamic properties of small clusters can be determined using the *ab initio* and Density Functional Theory (DFT) electronic structure methods widely applied in quantum chemistry. The term *ab initio* means “from first principles”; however, it does not mean that the Schrödinger equation is solved exactly. The fundamental idea of *ab initio* is to select a method that represents a reasonable approximation of the solution of the Schrödinger equation and then to choose a basis set that will implement the chosen method properly. The original Hartree-Fock (HF) method (Fock, 1930; Hartree, 1928) is incapable of providing a correct solution to the Schrödinger equation even if a very large and flexible basis set is employed. The difference in energy between the exact result and the Hartree-Fock limit energy is called the "correlation energy”. There are two classes of methods dealing with the “correlation problem”: variational methods including configuration-interaction models such as CID for doubly excited determinants, CISD for singly and doubly excited determinants and full CI and perturbation methods including MP*n*, where *n* is the maximum order of the correction term (Møller and Plesset, 1934), and the coupled cluster (CC) method (Cizek, 1966; Cizek and Paldus, 1971).

Perturbation MP2 method (Møller and Plesset, 1934) is a relatively economic way to perform the evaluation and it provides reasonable predictions of the correlation energy. Higher order/level methods are much more expensive and time consuming. MP4 with some terms removed to speed up the calculations, is often used. MP4 is somewhat more accurate but much more expensive than MP2. Coupled Cluster (CC), which is accurate but expensive and time consuming, is often used as a benchmark method.

The Density Functional Theory (DFT) describes the interacting electronic system via its density a one-body quantity instead of its many-body wave function, providing in this way accurate results comparable in quality with *Ab Initio* calculations at the MP2 level at lower computational costs. DFT is neither a Hartree-Fock method nor a post-Hartree-Fock method because the wave function in DFT is constructed in a different way (the energy functional is expressed in terms of electronic density) and the resulting orbitals are often referred to as "Kohn-Sham" orbitals (Kohn and Sham, 1965). The size and complexity of the systems that can be subject to a DFT treatment may range from a single atom to a complex system containing a few hundreds atoms. The choice of the energy functional is crucial for the reliability of the DFT method.

3.2 Density Functional Theory (DFT)

The historical roots of DFT can be traced to the 1920s with the so-called Thomas and Fermi (TF) theory (Fermi, 1927; Thomas, 1927) or the electronic energy theory based on the electron density distribution $n(r)$. This theory was found to be useful for describing some trends qualitatively, but not for any practical applications in chemistry and physics (Kohn, 1999). The most important feature of the TF theory is that it considers the interaction of electrons moving in an external potential $v(r)$ and provides a direct and simple relationship with the electron density distribution (Kohn and Sham, 1965).

$$n(r) = \gamma[\mu - v_{eff}(r)]^{3/2}, \qquad (3.2.1)$$

where

$$\gamma = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}, \qquad (3.2.2)$$

$$v_{eff}(r) \equiv v(r) + \int \frac{n(r')}{|r-r'|} dr', \qquad (3.2.3)$$

and μ is the r-independent chemical potential

After a series of developments it became clear that the TF theory was only a rough approximation to the exact solution of the many electron Schrödinger equation. The key problem was that while TF theory express quantities in terms in of $n(r)$, Schrödinger theory operates with $\Psi(r_1,...,r_N)$ and no clear connection between these two approaches was yet established (Kohn, 1999).

Another important feature of equation (3.2.1) is that $n(r)$ completely characterises the system and its integration will yield the total number of electrons in the system. These findings laid the basis for the modern DFT hypothesis, which states that "a knowledge of the ground state density of the $n(r)$ for any electronic system (with or without interactions) uniquely determines the system".

The next stage of DFT development was the Hohenberg-Kohn formulation (Hohenberg and Kohn, 1964). The principle lemma was that the ground state density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines the potential in a unique manner (Hohenberg and Kohn, 1964). Hohenberg-Kohn variational principle (Hohenberg and Kohn, 1964) is considered as the "exactification" of the Thomas-Fermi theory (Kohn, 1999), but its development did not solve the entire problems of TF theory and a major error due to the inadequate description of the kinetic energy remained to be improved (Kohn, 1999).

In 1965 Kohn and Sham introduced the so-called self-consistent Kohn-Sham orbitals and modified the DFT (Kohn and Sham, 1965). They concluded that a minimizing density $n(r)$ is given by a solution of the single particle equation:

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(r) - \varepsilon_j\right)\varphi_j(r) = 0, \qquad (3.2.4)$$

where $\varphi_j(r)$ is an eigenfunction and ε_j is an eigen value;
and the ground-state energy is given by:

$$E = \sum_j \varepsilon_j + E_{xc}[n(r)] - \int v_{xc}(r)n(r)dv - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}, \qquad (3.2.5)$$

The main issue in the Kohn-Sham theory is the calculation of the kinetic energy that is based on the assumption of non-interacting electrons. This assumption does provide ~99% of the energy. The remaining ~1% is due to the fact that in reality do electrons interact. This part of the kinetic energy is absorbed into an exchange/ correlation term, and thus the general DFT energy can be written as

$$E_{DFT} = T + E_{ne} + J + E_{xc}, \qquad (3.2.6)$$

where T is the kinetic energy, E_{ne} is the nuclear-electron interaction energy and J is the Coulomb energy term and E_{xc} is the remaining part of the energy after subtraction of the non-interacting kinetic energy (Jensen, 1999; Koch and Holthausen, 2001).

The accurate determination of the exchange-correlation term is a major problem of DFT (Jensen, 1999; Kohn, 1999). Therefore, a number of methods for calculating the exchange-correlation term have been suggested. These methods can be divided into two classes:

Local Density Models which are based on the Local Spin Density Approximation (LDA or LSDA)

The LDA is considered as the simplest way and the bedrock for almost all exchange-correlation approximations used currently in DFT. The LDA is based on the assumption of a uniform electron gas of density n (Kohn and Sham, 1965). The LDA exchange-correlation energy is given by:

$$E_{XC}^{LDA} = \int \varepsilon_{XC}(n(r))n(r)dr, \qquad (3.2.7)$$

where the $\varepsilon_{xc}(n)$ is the exchange-correlation energy per particle of a uniform electron gas of density n . The elementary exchange part is given by

$$\varepsilon_x(r) = -\frac{0.458}{r_s}, \qquad (3.2.8)$$

where r_s is the radius of a sphere consisting of one electron this being and calculated by

$$\left(\frac{4\pi}{3}\right) r_s^{\ 3} = n^{-1}, \qquad (3.2.9).$$

On the other hand, a correlation was initially proposed in 1938 by Wigner (Wigner, 1938) and given by

$$\varepsilon_c = -\frac{0.44}{r_s + 7.8}, \qquad (3.2.10)$$

but subsequently the correlation term has been improved to reach ~ 1% precision by Ceperley, (Ceperley, 1978) and Ceperley and Alder (Ceperley and Alder, 1980). In the same year Vosko, Wilk, and Nusair (Vosko et al, 1980) reported a number of correlation functionals which are known by their initials as (VWN). Currently, these functionals are implemented in a number of software packages. The most recently introduced and considered to be the most accurate correlation functions were developed by Perdew and Wang (Perdew and Wang, 1992) or by Hertwig and Koch, (Hertwig and Koch, 1997).

The LDA approximation is only a rough estimate since it is based on the assumption that the electron density is constant for the uniform electron gas, and this dearly is not the case in actual systems. Consequently, one must wonder about the reliability of results obtained with such a crude model. Surprisingly, a number of studies show that the LDA model can deliver results which are comparable or even better to Hartree-Fock approximation (Koch and Holthausen, 2001).

Generalized Gradient Approximations (GGA)

GGA sometimes also called Gradient Corrected Methods or non-local methods. In principle, these methods can be considered as an extension and improvement of the LDA since they include non-homogeneity of the electron density and exchange-correlation energy term that depends not only on the electron density but also on the derivatives of the density providing an estimate of the gradient of the charge density (Jensen, 1999; Koch and Holthausen, 2001). The Taylor series expansion of the uniform density was used and having the LDA term as the first term of the series and the result is given by:

$$E_{XC}^{GEA}\left[\rho_\alpha,\rho_\beta\right]=\int\rho\varepsilon_{XC}\left(\rho_\alpha,\rho_\beta\right)d\vec{r}+\sum_{\alpha,\beta}\int C_{XC}^{\alpha,\beta}\left(\rho_\alpha,\rho_\beta\right)\frac{\nabla\rho_\alpha}{\rho_\alpha^{2/3}}\frac{\nabla\rho_\beta}{\rho_\beta^{2/3}}d\vec{r}+\dots, \qquad (3.2.11)$$

where ρ is electron density, $\nabla\rho\left(\vec{r}\right)$ is the gradient of the charge density and α and β indicate the electron spin. This functional is also called the gradient expansion approximation (GEA) (Koch and Holthausen, 2001).

Initially GEA was expected to provide a better approximation of the exchange-correlation functional but unfortunately the application of GEA has not lead to the desired accuracy and its performance is typically worse than the simple LDA. Koch and Holthausen linked the failure of GEA with the lose of the physical properties associated with exchange-correlation hole that exists in the LDA functional (Koch and Holthausen, 2001). For example, the exchange hole in GEA is no longer required to be negative for any pair and this leads to the loss of the dependence between the depth of the on-top hole and its extension. In order to solve this problem, the exchange-correlation holes need to be truncated that $h_X(\vec{r}_1;\vec{r}_2)$ and $h_C(\vec{r}_1;\vec{r}_2)$ will contain 1 and 0 electron charge, respectively. As a result, a new functional that includes the charge density gradients and constrained holes restored was obtained. This functional is known as the generalized gradient approximation (GGA). The GGA, which is considered as the core of the modern density functional theory, is given by:

$$E_{XC}^{GGA}\left[\rho_\alpha,\rho_\beta\right]=\int f\,(\rho_\alpha,\rho_\beta,\nabla\rho_\alpha,\nabla\rho_\beta)d\vec{r}\,, \qquad (3.2.12)$$

E_{XC}^{GGA} functional that consists of two parts (exchange and correlation), can be expressed as

$$E_{XC}^{GGA}=E_{X}^{GGA}+E_{C}^{GGA}\,, \qquad (3.2.13)$$

A number of methods have been established in order to provide an accurate estimation of the contribution of the exchange and correlation parts such as BP86 (Becke, 1986; Perdew, 1986), PW91 (Becke, 1988; Perdew et al, 1992), PBE (Perdew et al, 1996) and FT97 (Filatov and Thiel, 1997). Unfortunately, there is no systematic approach used in these methods in general and they are commonly evaluated based on their performance, results and whether they satisfy the boundary conditions of the hole functions. Moreover, most of these methods include semiempirical functionals that consist of terms calibrated against reference or experimental values rather than actually derived from first principles (Koch and Holthausen, 2001). On the other hand, there are some methods, which are free of such semiempirical terms such as the PBE method (Perdew et al, 1996).

Since there are a large number of density functionals, it is practical to focus on the particular methods that were used in this study. The PW91 method (Perdew et al, 1992) consists of two parts. The exchange part, which is quite similar to that proposed by Beck in 1988 and known as B88 (Becke, 1988), Jensen (Jensen, 1999) has rewritten the formula as:

$$\varepsilon_X^{PW91}=\varepsilon_X^{LDA}\left(\frac{1+xa_1\sinh^{-1}(xa_2)+(a_3+a_4e^{-bx^2})x^2}{1+xa_1\sinh^{-1}(xa_2)+a_5x^2}\right), \qquad (3.2.14)$$

where $a_{1\text{-}5}$ and b are suitable constants and $x=\dfrac{|\nabla\rho|}{\rho^{4/3}}$

The correlation part is given by:

$$\varepsilon_C^{PW\,91}=\varepsilon_C^{LDA}+\Delta\varepsilon_C^{PW\,91}, \qquad (3.2.15)$$

where $\Delta\varepsilon_C^{PW\,91}$ is given by:

$$\varepsilon_C^{PW\,91}[\rho] = \rho\left(H_o(t, r_S, \zeta) + H_1(t, r_S, \zeta)\right), \tag{3.2.16}$$

where,

$$H_o(t, r_S, \zeta) = b^{-1} f(\zeta)^3 \ln\left[1 + a\frac{t^2 + At^4}{1 + At^2 + A^2t^4}\right], \tag{3.2.17}$$

and

$$H_1(t, r_S, \zeta) = \left(\tfrac{16}{\pi}\right)(3\pi^2)^{1/3}\left[C(\rho) - c\right] f(\zeta)^3 t^2 e^{-ax^2/f(\zeta)^2}, \tag{3.2.18}$$

where

$$f(\zeta) = \frac{1}{2}\left((1+\zeta)^{2/3} + (1-\zeta)^{2/3}\right), \tag{3.2.19}$$

$$t = \left(\tfrac{192}{\pi^2}\right)^{1/6} \frac{|\nabla\rho|}{2f(\zeta)\rho^{7/6}}, \tag{3.2.20}$$

and

$$A = a\left[e^{-b\varepsilon_C(r_S,\zeta)/f(\zeta)^3} - 1\right]^{-1}, \tag{3.2.21}$$

where $\varepsilon_C(r_S, \zeta)$ is the PW91 parameterization of the LDA correlation energy functional, x has been defined earlier in equation (2.3.14), a, b, c, d are suitable constants and

$$C(\rho) = b_1 + \frac{b_2 + b_3 r_S + b_4 r_S^2}{1 + b_5 r_S + b_6 r_S^2 + b_7 r_S^3}, \tag{3.2.22}$$

where b_{1-7} are numerical constants

Hybrid Functionals

The concept of hybrid functions appeared due to the relatively large contribution of the exchange function compared to the correlation part and possibility of calculating the exact exchange energy of a Slater determinant. It was anticipated that the accuracy of the energy of the exchange-correlation functional

$$E_{XC} = E_X^{HF(Exact)} + E_C^{KS}, \qquad (3.2.23)$$

where the E_X^{HF} is given by:

$$E_X^{HF} = \frac{1}{2}\iint \frac{\rho_{\circ}^{HF}(\vec{r}_1)\,\mathrm{h}_X^{HF}(\vec{r}_1;\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2, \qquad (3.2.24)$$

would be significantly increased: Unfortunately, this direct combination of the Hartree-Fock exact exchange function and the approximate Kohn-Sham (KS) correlation did not reach the desired accuracy. In the case when it is applied to chemical bonding, the error is 6-7 times higher than that of KS exchange-correlation approximations (Koch and Holthausen, 2001). The main reason for this failure is the presence of the enharmonic effect in the exchange-correlation functional, which appears because the exact delocalized exchange hole is combined with a localized model hole for correlation. Therefore, the cancellation between both individual holes cannot occur, and this leads to the erroneous characterisation of the total hole.

Becke (Becke, 1993a; Becke, 1993b) suggested an approach, where hybrid functionals were used. Becke's approach is based on integrated exchange-correlation hole of coupling-strength and this term, which is equivalent to the exchange-correlation in the Kohn-Sham scheme, is given by:

$$E_{XC} = \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\bar{h}_{XC}(\vec{r}_1;\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 , \tag{3.2.25}$$

$$= \int_0^1 E_{ncl}^{\lambda} d\lambda , \tag{3.2.26}$$

where λ is the coupling strength parameter and the integration over λ reveals the non-classical contribution to the electron-electron interaction for different values of λ and introduces the kinetic energy contribution into the E_{XC} and E_{ncl} corresponds to the pure potential energy which depends on λ.

Investigation of the integral of E_{ncl}^{λ} limits reveals that at $\lambda = 0$, the system converts to an non-interacting system lacking, at the same time, the antisymmetry of the fermion wave function from the classical term that leads to pure exchange E_{ncl}^{λ}, which is simply the exchange term of a Slater determinant. This term can be calculated exactly, when the KS orbitals are available.

At the other end of the integral, when $\lambda = 1$ the system converts to be fully interacting and non-classical terms will include both the exchange and correlation contributions. This term can be obtained with a satisfactory level of accuracy by using any approximation of the E_{XC} functionals. In order to fully evaluate this integral, it is necessary to account for all intermediate values of λ. Currently, no approximation is available for this purpose, therefore, we need to use a different approach to tackle this information gap, but first it is necessary to recall some important points (Koch and Holthausen, 2001):

1. The LDA and GGA holes models are reference point centred and localized and they do not provide a full description of the left-right correlation.

2. At $\lambda = 0$, the system becomes purely exchange with delocalized holes and no information about the localized model holes is available.

Consequently, it is clear that if we need to establish a complete description of the holes model at $\lambda = 0$, it is necessary to add in a certain amount of a pure exchange function. Based on this conclusion different models have been developed starting from the simple linear approximation of E_{ncl}^{λ} function and leading to the so-called Half and Half combination (HH) which given by:

$$E_{XC}^{HH} = \frac{1}{2} E_{XC}^{\lambda=0} + \frac{1}{2} E_{XC}^{\lambda=1}, \qquad (3.2.27)$$

The main product in this approach was an exchange-correlation functional developed by Becke (Becke, 1993b) where a set of semiempirical coefficients to determine mix ratios of different components were introduced

$$E_{XC}^{B3} = E_{XC}^{LSDA} + a(E_{XC}^{\lambda=0} - E_{X}^{LSDA}) + b\Delta E_{X}^{B88} + c\Delta E_{C}^{PW91}, \qquad (3.2.28)$$

where a, b, and c are constants controlling the contributions of the exchange and correlation gradient corrections to the local density approximation, and they have been optimally parameterized based on the G2 database and total energies to the following values, $a = 0.20$, $b = 0.72$ and $c = 0.81$, E_{X}^{B88} is the exchange term proposed by Becke (Becke, 1988) and E_{c}^{PW91} is the Perdew-Wang's correlation functional (Perdew and Wang, 1992).

Stephens (Stephens et al, 1994) proposed a similar combination but replaced the correlation functional of Perdew-Wang's with Lee, Yang and Parr (LYP) (Lee et al, 1988) correlation functional and they utilized the exact a, b and c parameters and then the function converted to the popular B3LYP functional being given by:

$$E_{XC}^{B3LYP} = (1-a)E_{X}^{LSD} + aE_{XC}^{\lambda=0} + bE_{X}^{B88} + cE_{C}^{LYP} + (1-c)E_{C}^{LSD}, \qquad (3.2.29)$$

where the E_C^{LYP} is given by:

$$E_C^{LYP} = -a\frac{\gamma}{(1+d\rho^{-1/3})} - ab\frac{\gamma e^{c\rho^{-1/3}}}{9(1+d\rho^{-1/3})\rho^{8/3}} \\ \mathrm{x}\begin{bmatrix} 18(2^{2/3})C_F(\rho_\alpha^{8/3}+\rho_\beta^{8/3})-18\rho t_W \\ +\rho_\alpha(2t_W^\alpha+\nabla^2\rho_\alpha)+\rho_\beta(2t_W^\beta+\nabla^2\rho_\beta) \end{bmatrix}, \tag{3.2.30}$$

where γ is given by:

$$\gamma = 2\left[1-\frac{\rho_\alpha^2+\rho_\beta^2}{\rho^2}\right], \tag{3.2.31}$$

and t_W^σ is known as the local Weizsacker kinetic energy density being given by:

$$t_W^\sigma = \frac{1}{8}\left(\frac{|\nabla\rho_\sigma|^2}{\rho_\sigma} - \nabla^2\rho_\sigma\right), \tag{3.2.32}$$

and a, b, c, d parameters are determined by fitting to Helium atom data.

4 AIMS OF THE STUDY

The purpose of this study is to obtain an understanding at the molecular nature into the micro-level framework of atmospheric aerosol chemistry and physics. The main goals of this study were:

1. To compute different molecular level properties such as dipole moment and thermodynamics properties of different clusters and to integrate the outcome into micro-level atmospheric models. In this case, the focus was on the structure and dipole moments of sulfuric acid hydrates and their effect on the uptake coefficient for charged nano-sized particles and subsequent nucleation rates.

2. To reproduce parts of the atmospheric or laboratory systems based on first principles in order to understand the formation mechanisms and key factors controlling the particle formation. Here the focus was on the formation and transformation of nitric acid hydrates under stratospheric conditions and the effect of the chemical identity of core ions on the sign preference phenomena.

5 RESULTS and DISCUSSION

Intermolecular interactions are the key to the cluster formation mechanisms. In chapter two it was stated that most of the nucleation theories and models suffer from inaccuracies in describing the molecular level properties. Recently, Nadykto and Yu (Nadykto and Yu, 2004b) have developed a model describing the effect of the cluster electrical properties and dipole moment in particular on how this helps in estimating the uptake coefficient. The dipole moment is directly related to the charge distribution and the geometry of the molecular cluster. Therefore, clusters with similar chemical constituents will have different dipole moments. The dipole moment is a dimensional quantity. Paper I provides a detailed description of the dipole moment of clusters composed of the sulfuric acid and water. Dipole-dipole interactions are the main intermolecular forces in those clusters. The overall dipole moment of the clusters can be determined based on the orientation of the constituent molecules (sulfuric acid and water). Figure (5.1) reveals the variation of sulfuric acid mono-, di- and trihydrates. It is clear that an increase in the numbers of water molecules does not affect the polarity of the cluster. The main factor effects the dipole moment is the distribution of the water molecules around the sulfuric acid molecule. Therefore, one can see from figure (5.1) that a monohydrates cluster will have a higher dipole moment than di- or trihydrates clusters.

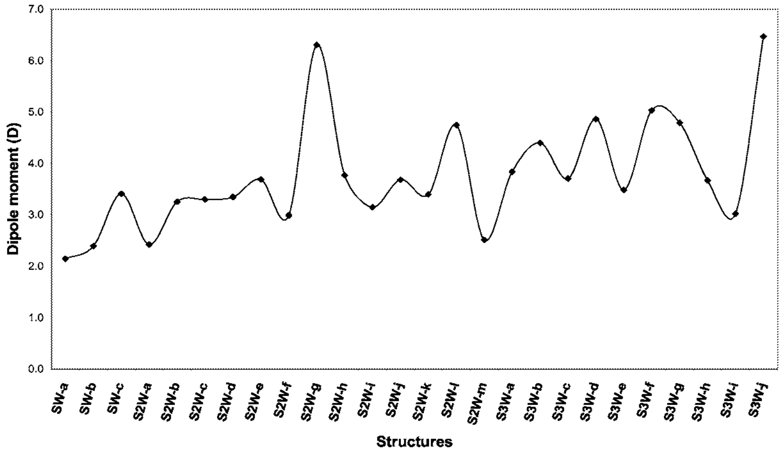


Figure 5.1 Changes of dipole moment with molecular structures of sulfuric acid hydrates

The calculated dipole moments in paper I were used to predict the effect of the molecular structures of sulfuric acid and its mono-, di, trihydrates on the uptake of molecules and molecular clusters by charged cluster/ultrafine particles. The dipole moments were directly used in the calculation of the enhancement factor (EF) developed recently by Nadykto and Yu (Nadykto and Yu, 2004b) and given by:

$$EF = 1 + \frac{2lE(r_p + r_m)L\left(\frac{lE(r_p + r_m)}{kT}\right) + \alpha\varepsilon_\circ E^2(r_p + r_m)}{3kT} \qquad (5.1)$$

where r_p is the particle radius , r_m is the radius of the gas molecule, k is the Boltzmann constant, T is the ambient gas temperature, l is the dipole moment of the gas molecule, $L(z) = \left[\frac{e^z + e^{-z}}{e^z - e^{-z}}\right] - \frac{1}{z} = \langle\cos\theta\rangle$ is the Langevin function (Loeb, 1961), θ is the angle between the dipole and the electrical field of the charged particle/cluster, α is the polarizability, $\varepsilon_\circ$ is the vacuum permittivity, $E(r) = \frac{e_\circ}{4\pi\varepsilon_\circ r^2}$ is the electrical field in the vicinity of the charged particle and $e_\circ$ is the elementary charge.

Then the (EF) was used in calculating the uptake coefficient, which is computed as the Brownian coagulation kernel (K_{mp}) (Fuchs, 1964) between polar molecules/molecular clusters and charged cluster/particles in the free regime.

$$K_{mp} = EF\pi(r_p + r_m)^2\sqrt{\bar{V}_p^2 + \bar{V}_m^2} \qquad (5.2)$$

The study revealed the strong effect of the molecular dipole moment on the uptake rate, which could reach as much as ~230 %. Figure (5.2) illustrates the different uptake coefficients related to various molecular structures of sulfuric acid mono-, di-, and trihydrates.

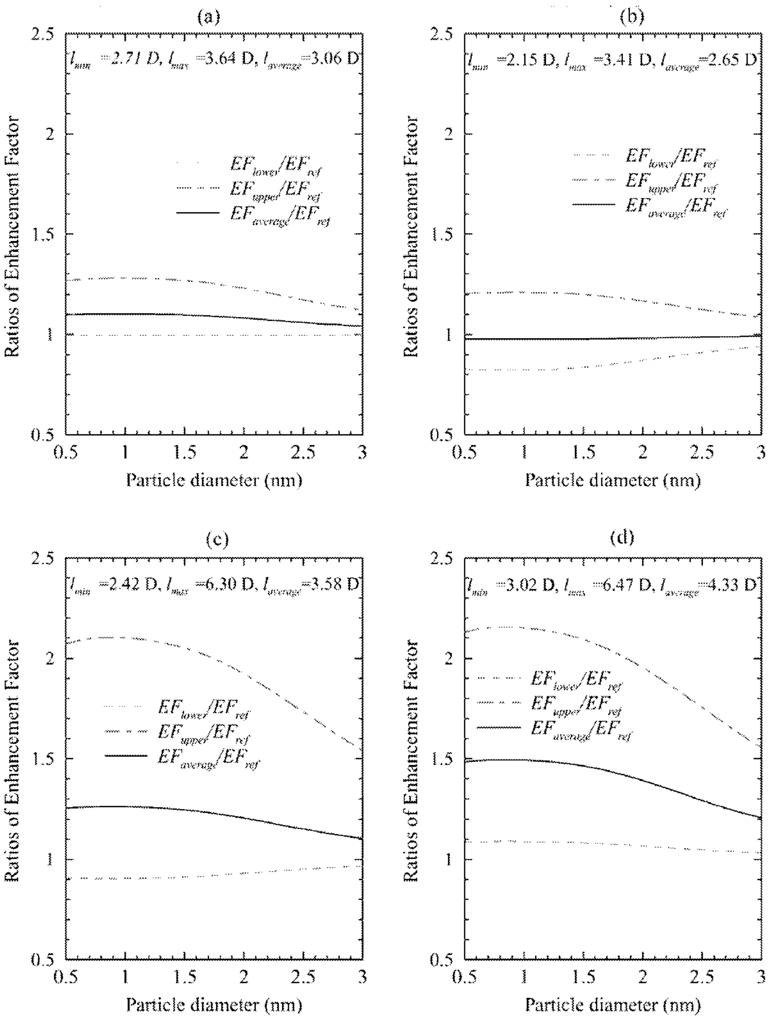
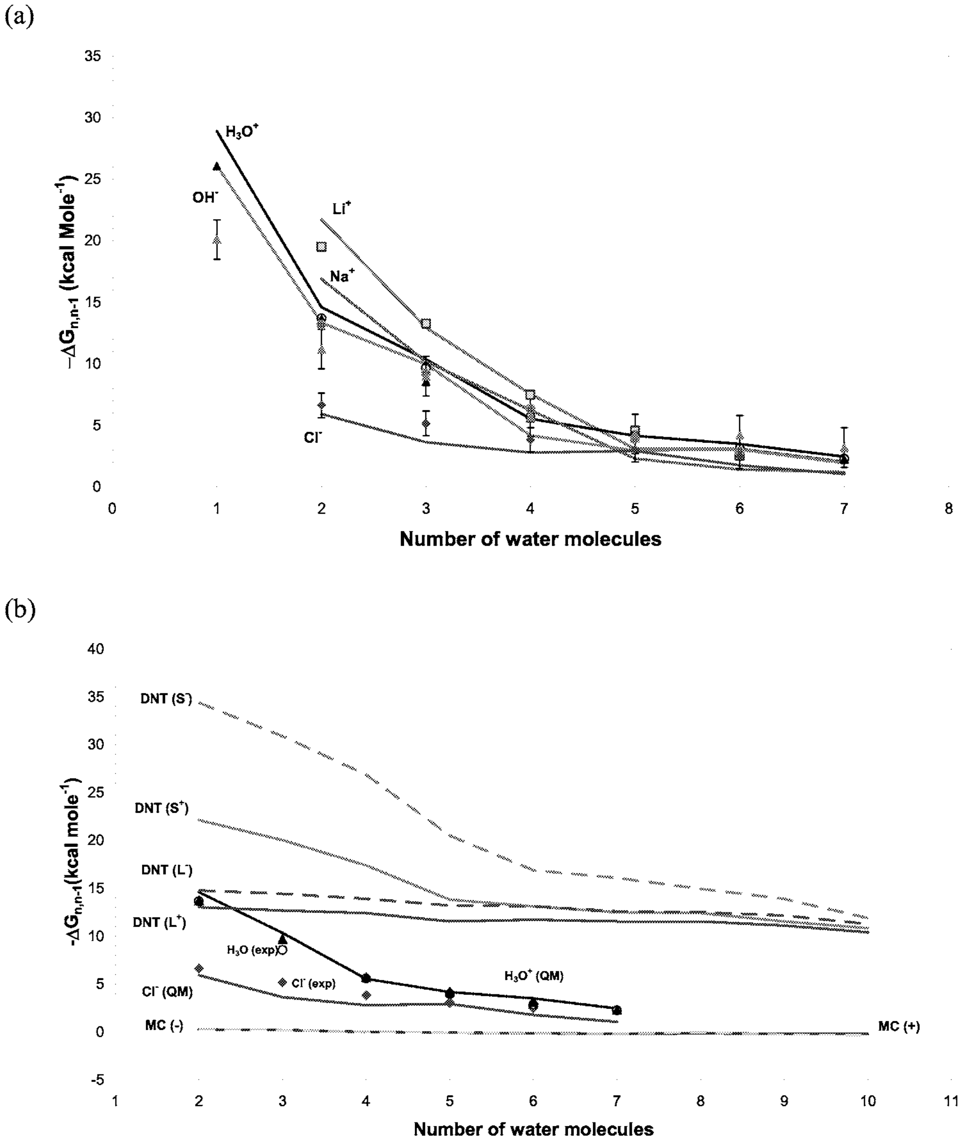


Figure 5.2 The upper and lower limits of the ratio between the uptake coefficients calculated using the maximum and minimum values of the dipole moments (EF_{upper}, EF_{lower}) and those (EF_{ref}) calculated using the reference measured value of the dipole moment of sulfuric acid (2.74 D; Kuczkowski et al. 1981) for (a) free sulfuric acid molecules, (b) monohydrates, (c) dihydrates, and (d) trihydrates. *The figure has been re-produced with kind permission from AS&T.*

The presence of ions helps to overcome the potential barrier and to increase the rate of formation of critical ionic clusters (embryos). Ion-induced nucleation experiments have shown that in a variety of systems, there may be different nucleation rates for positive and negative ions. This phenomenon, known as the sign preference, remains mysterious, despite being investigated in considerable detail in the last decades, this phenomenon remain.

Figure (5.3) shows the changes in Gibbs free energy calculated in this study and early calculated values using different theories (Monte-Carlo (MC) simulations (Oh et al, 2001), or the Dynamic Nucleation Theory (DNT) (Kathmann et al, 2005)) in addition to experimentally measured values.



(c)

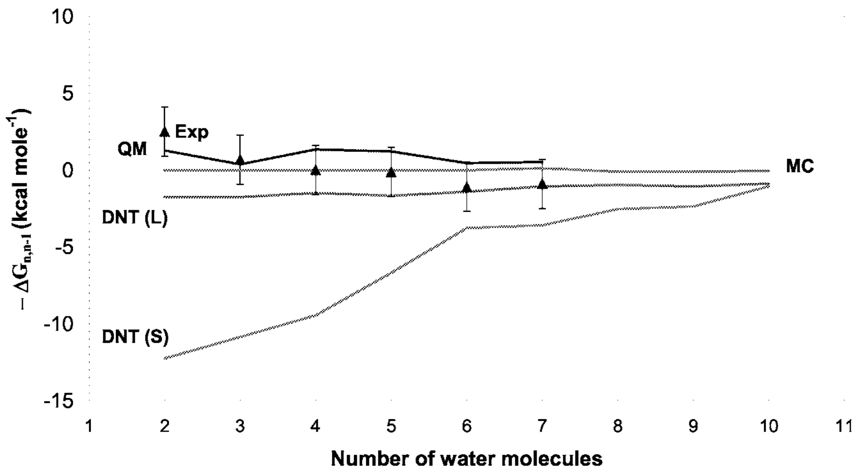


Figure 5.3 Comparison of experimental and theoretical values of the Gibbs free energy ΔGn,n-1 for $X^{\pm}(H_2O)_{n-1} + H_2O = X^{\pm}(H_2O)_n$ reactions (a),(b), and the difference in the Gibbs free energy $\Delta G(j)$ between j-mers formed over core ions of opposite sign (water cation and water anion) (c). Curves and symbols of the same colour refer to theoretical results and experimental data, respectively. Abbreviations DNT, MC and QM refer to the Dynamic Nucleation Theory (Kathmann et al, 2005), Monte-Carlo study (Oh et al, 2001) and present study, respectively. Symbols L and S refer to core ions of indeterminate composition of 0.1 nm and 1 nm radius, respectively (Kathmann et al, 2005). Subscripts "+" and "-" refer to the charge polarities. Experimental data for Li-$(H_2O)n$ (Dzidic and Kebarle, 1970), Na+$(H_2O)n$ (Dzidic and Kebarle, 1970) , OH-$(H_2O)n$ (Meotner and Speller, 1986), H_3O+ $(H_2O)n$ (Froyd and Lovejoy, 2003; Kebarle et al, 1967) and Cl-$(H_2O)n$ (Hiraoka and Mizuse, 1987) were used. Experimental values of $\Delta G(j)$ (blue triangles in Fig. 5.3 (c) were calculated from the experimental data for H_3O+ $(H_2O)n$ (Froyd and Lovejoy, 2003) and OH-$(H_2O)n$ (Meotner and Speller, 1986). The calculations were performed at an ambient temperature of 298.15 K and ambient pressure of 101.3 KPa.

The strong effect of the chemical nature of the core ion on the conversion of vapor molecules to clusters is essentially quantum in nature, and thus, systematic accounting for the actual core species is impossible without taking into account the actual electronic structures of the core ions. Ignorance or approximation of the actual electronic structure, which is the key parameter controlling the sign preference, e.g. by using oversimplified electrostatic models, leads to the failure of the existing nucleation theories (Brodskaya et al, 2002; Kathmann et al, 2005; Kusaka et al, 1995a; Kusaka et al, 1995b; Nadykto and Yu, 2003; Oh et al, 2001; Warshavsky and Zeng, 2002).

Quantum theory properly accounts for the chemical identity of the core ion. Unlike the existing nucleation models (Brodskaya et al, 2002; Kathmann et al, 2005; Kusaka et al, 1995a; Kusaka et al, 1995b; Nadykto and Yu, 2003; Oh et al, 2001; Warshavsky and Zeng, 2002), which are very sensitive to poorly defined input parameters, quantum theory can be applied to a system with an arbitrary chemical composition.

In paper III, the hydration energies and sign preference for water were investigated, using quantum mechanics and it was shown that the sign preference is decided at very early stages of the cluster growth. We demonstrated that the negative sign preference for water suggested in earlier theoretical studies (Kulmala, 2003; Laakso et al, 2004; Lee et al, 2003; Yu and Turco, 2000) is in contradiction to both our model predictions and to the experimental data. We found that application of simplified models of electrostatic interactions not specifying the electronic structure of the seed ion would result in the failure of molecular nucleation models. On the other hand, a rigorous treatment based on the quantum mechanics (QM) of the electronic structures and the interaction energies was found to lead to good agreement of the model predictions with the experimental data. This study suggests that quantum DFT is reliable and affordable analytical tool for the studies of the thermodynamics of the ion-induced nucleation.

Papers IV and V discuss the formation pathways of NAD and NAT which are forming the PSCs crystals. The surfaces of those crystals are the site for heterogeneous chemical reactions, leading to the activation of the chlorine and subsequently to ozone depletion.

Paper IV presents for the first time a second NAT molecular structure, the so called α-NAT and demonstrates the transformation process between the two NAT modifications. Figure (5.4) presents the two transformation pathways which were identified. The first transformation pathway is a direct transformation between the α- and β-NAT and the second is the pathway through the fourth-order of nitric acid hydrates (NA4). The second pathway was more favorable thermodynamically due to its lower energy barrier. The results obtained in this study are in agreement with other published observations (Koehler et al, 1992; Tizek et al, 2004).

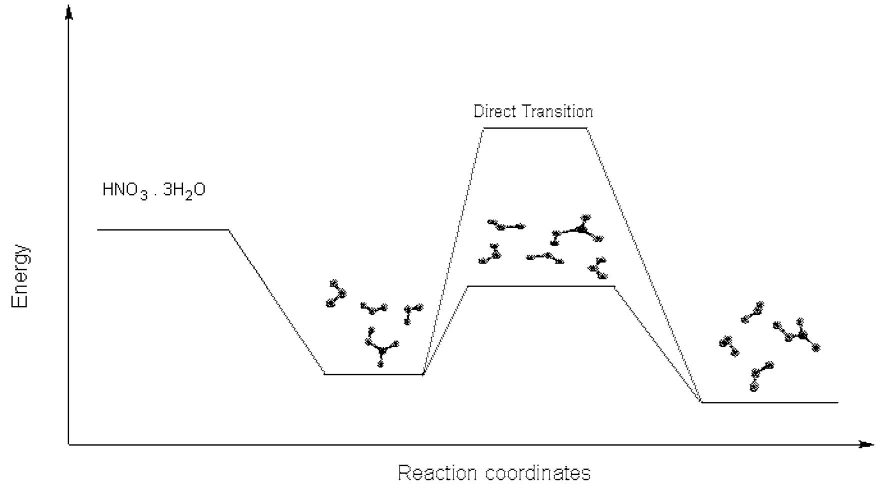


Figure 5.4 Schematic diagram of the transformation pathways from α-NAT to β-NAT

Paper V is focused on the possibilities for formation of NAD and NAT modification under stratospheric conditions. This study first explains the formation pathway of different NAD and NAT conformations based on their thermodynamic properties. In addition, two new molecular conformations of NAD have been reported. The data presented in paper V indicates that the crystals in PSCs most likely consist of mixed phase of NAD and NAT.

Figure (5.5) shows the formation pathways of nitric acid dihydrates and trihydrates. As seen from the figure (5.5), the most favorable formation pathway is the NAM→ α-NAD →α-NAT at 185 K temperature and 0.1 atm pressure.

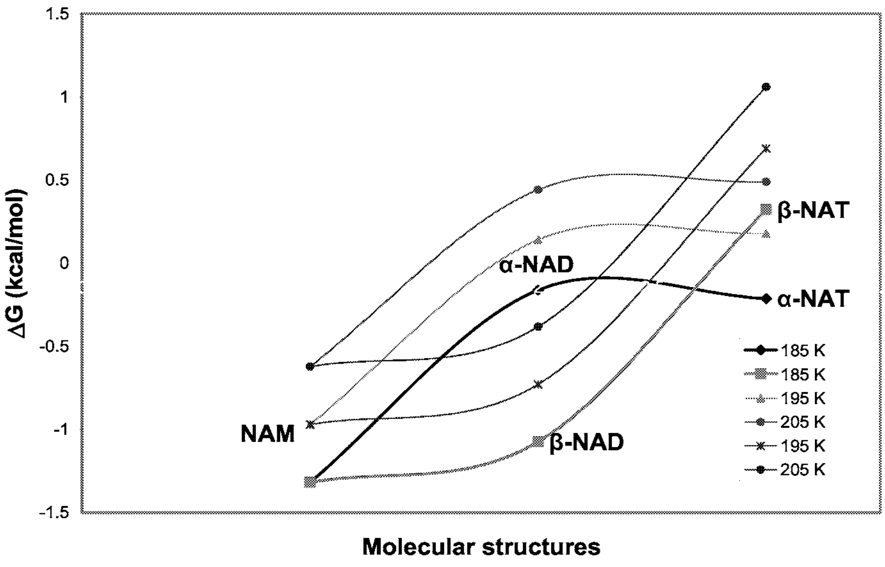


Figure 5.5 Changes in formation energies of α and β-NAT at different temperatures

6 CONCLUSIONS

The main general conclusion of this thesis is that the quantum mechanics approach can be particularly useful for understanding atmospheric reactions and for elucidating the factors influencing aerosol particle formation.

It was found that the different molecular structures of the same chemical composition may have different electrical properties e.g. different dipole moments. This difference can be traced back to the dipole-dipole, dipole-induced-dipole or induced-dipole-induced-dipole interactions between the molecules in the cluster. Short-range electrical properties of small clusters have a direct effect on their uptake coefficients and can account for as much as a 230% difference for a cluster of the same chemical constituent.

We have solved the problem of the sign preference, a phenomenon that has remained a mystery for more than a century. We determined that the effect of the chemical nature of the core ion on the transformation of vapor molecules in the clusters is quantum in nature, and therefore, one cannot account for the actual core species without taking into account the actual electronic structures of the core ions. Ignoring this fact or using only a crude approximation of the actual electronic structure, which is the key parameter controlling the sign preference, with oversimplified electrostatic models, is the reason for the failure of existing nucleation theories. The influence of the core ion on the n-mer formation free energy is associated mainly with the first few growth steps, where the effect of the core ion properties on the cluster thermodynamics is very large. This means that an answer to the practical question "Which ion is the better nucleator?" can be obtained by carrying out a quantum mechanics study, or by examining the data of the thermochemistry for cluster ions available for a number of substances.

The quantum mechanics approach was proven again as an efficient tool to track the formation of nitric di-, and trihydrates and their transformation. NAD and NAT are the building blocks of the PSCs crystals, the surfaces of which can be considered as the stage where the heterogeneous chemical reactions occur, leading to chorine activation and ozone depletion. In this study, new molecular structures of NAD and NAT have been identified the so called α-NAD and α-NAT forms. It was demonstrated that the thermodynamics evaluation of the different NAD and NAT clusters indicates that the PSCs crystals are would be expected to form from a mixture of both β-NAD and β-NAT molecular modifications.

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