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The role of positive cluster ions during new particle formation
events in the CERN CLOUD chamber simulating Asian
tropopause conditions

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Abstract

Earth's climate is influenced by many different factors, aerosols being one of them. They can absorb and scatter radiation which passes through the atmosphere and initiate cloud formation. Both of these processes have direct influence on the global mean surface temperature. Despite the critical role they are playing, many questions regarding their climate impact remain. Aerosol particles can enter the atmosphere in various ways. One of them is new particle formation. This process describes the production of particles by nucleation of trace gases. Models suggest, that about half of the atmospheric particles arise by new particle formation, which demonstrates the significance of the process. Some trace gases are known to play a critical role in new particle formation, but for many other species the question of their involvement remains uncertain. This thesis investigates new particle formation involving sulfuric acid, ammonia, and glyoxal. These trace gases reflect the system which is found in the Asian Tropopause Aerosol Layer (ATAL). The ATAL has enhanced particle concentrations for its altitude, due to the deep convective uplifting of the Asian summer monsoon and can be recreated and studied in the CERN CLOUD chamber. The new particle formation processes have been investigated under various aspects with an Atmospheric Pressure interface Time of Flight Mass Spectrometer (APi-ToF MS). The study discovered that glyoxal suppresses nucleation induced through positive ions. Still, enhanced particle concentrations were found compared to a system without glyoxal, indicating an increased formation rate by other nucleation mechanisms.

Zusammenfassung

Das Klima der Erde wird von vielen verschiedenen Faktoren beeinflusst. Aerosole sind eine wichtige Komponente in diesem System. Sie können Strahlung auf dem Weg durch die Atmosphäre absorbieren und streuen, sowie Wolkenbildung initiieren. Diese Prozesse haben einen direkten Einfluss auf die globale Durchschnittstemperatur an der Erdoberfläche. Trotz ihres hohen Stellenwerts, gibt es zum Einfluss der Aerosole auf das Klima noch viele offene Fragen. Eine Art wie Aerosole in die Atmosphäre gelangen, ist über die Partikelneubildung. Dieser Prozess beschreibt das Entstehen neuer Partikel durch das Zusammenkommen von Spurengasen (Nukleation). Schätzungen zufolge entstehen ungefähr die Hälfte der Partikel der Atmosphäre durch diese Prozesse, was ihre erhebliche Relevanz unterstreicht. Zwar ist schon für einige Spurengase bekannt, dass sie eine signifikante Rolle für die Partikelneubildung spielen, jedoch ist bei vielen anderen Spezies die Frage noch offen, wie sie in diese Prozesse involviert sind. Diese Arbeit widmet sich den Prozessen der Partikelneubildung von Schwefelsäure, Ammoniak und Glyoxal. Diese Komponenten spiegeln die Gegebenheiten in der Aerosolschicht der asiatischen Tropopause (ATAL) wieder, in der vermehrte Partikelkonzentrationen in den höheren Lagen zu beobachten sind. Ein solches System konnte in der CLOUD Kammer am CERN nachgestellt und untersucht werden. Die Partikelneubildung mittels positiver Ionen wurde anhand eines Atmospheric Pressure interface Time of Flight Mass Spectrometers (APi-ToF MS) unter verschiedenen Gesichtspunkten analysiert. Es konnte herausgefunden werden, dass Glyoxal das Wachstum positiver Nukleationskerne hemmt. Jedoch werden mehr Partikel gebildet im Vergleich zu einem ebensolchen System ohne Glyoxal, was auf einen Anstieg der Produktion durch einen anderen, noch nicht identifizierten Prozess hinweist.

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1. Introduction

One of the biggest challenges today's society is confronted with is the man-made climate change. The rapid increase of global mean surface temperature is leading to ecosystems being altered irreversibly and extreme weather phenomena becoming normality. Strips of land become uninhabitable and humans die prematurely. [1]

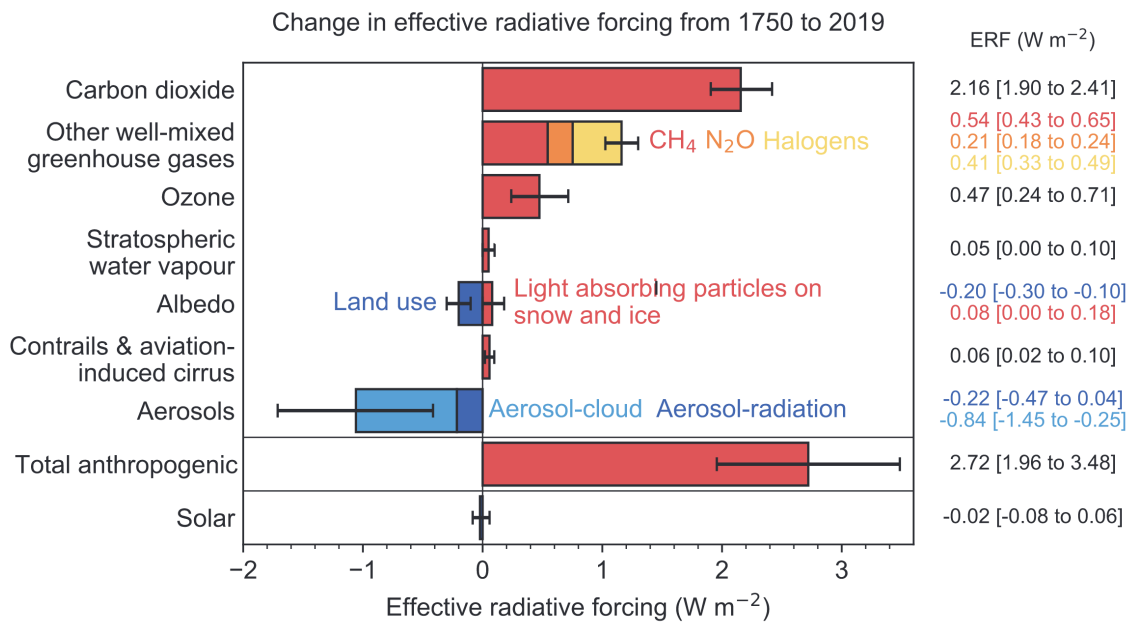


Figure 1.1.: Radiative forcing of different forcing agents in W/m^2 . [1]

Atmospheric aerosols play a significant role for the changing climate. Figure 1.1 depicts the change in effective radiative forcing of different forcing agents from 1750 in comparison to 2019. 1750 is chosen as a reference period for its pre-industrial character. With the subsequent industrial revolution, the significant anthropogenic influence on the earth's atmosphere began. Radiative forcing measures the change in the atmosphere's radiation balance upon external perturbation of the system. Warming of the earth comes about through a positive radiative forcing, and cooling through a negative [2]. It is prominent, that aerosols have a strong cooling effect, though the uncertainty of their

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actual impact is the biggest among the key players. This implies a knowledge gap on atmospheric aerosols which needs to be closed in order to take measures and mitigate climate change. [1]

The atmospheric aerosol particles can be divided into two categories, primary and secondary particles. Primary particles are emitted into the atmosphere directly, like mineral dust or sea spray particles. In contrast, secondary particles are formed in the atmosphere itself through nucleation of precursor gases [3]. Models suggest that almost half of the cloud-forming particles (also called cloud condensation nuclei (CCN)) found in the atmosphere are of secondary nature [4, 5, 6, 7]. Though the micro physical properties of atmospheric new particle formation (NPF) has been investigated thoroughly in the last decades [5, 8, 9], many aspects are still unknown.

It has been known for decades that ions play an important role in new particle formation [10]. Throughout the 20th century, experiments have been carried out, quantifying the effect of ions on NPF. It was shown, that ions enhance the nucleation rate (number of particles forming per second per unit volume) substantially [11]. The question of how ions influence atmospheric aerosol particle formation inspired the CERN CLOUD (Cosmic Leaving Outdoor Droplets) experiment, lead by Jasper Kirkby. The experiment was designed to investigate the link between climate and cosmic rays, which are a major source of ions in our atmosphere [12, 13].

One factor which makes understanding NPF in our atmosphere more complex is the variability between different regions. Atmospheric systems differ for locations and altitudes, leading to divers mechanisms that dominate NPF [14]. One example is the Asian Tropopause Aerosol Layer (ATAL). The enhanced concentrations of particles in the Asian tropopause were first recognized by satellite measurements in the late 2000s [15]. It was found that the Asian summer monsoon enables efficient transport of particles and precursor gases up to around 13 to 18 km altitude. Studies revealed the composition of ATAL to be around 60 % organics by mass, one of the compounds being glyoxal [16, 17]. Glyoxal is a product of oxidation of volatile organic compounds (VOC). VOCs in turn are emitted by anthropogenic sources as well as by biogenic ones. It is known that one of glyoxals main sinks is aerosol uptake, which suggests that it may affect NPF processes [18]. This motivated the experiments carried out during the CLOUD17 measurement campaign in the fall of 2024 at the CERN CLOUD chamber, which investigated NPF processes with glyoxal.

Besides other instruments, the University of Vienna provisioned an Atmospheric Pres-

sure interface Time of Flight Mass Spectrometer (APi-ToF MS) for the campaign. The APi-ToF ran in positive ion mode, which effectively allows the measurement of positive cluster ions. These cluster ions are of critical interest for the NPF events, as they reveal information about the chemical composition of nucleating embryos, giving insights into what the NPF mechanism is based upon.

This thesis analyzes the data collected with the positive APi-ToF during the glyoxal experiments carried out at the CLOUD chamber. The data was explored in reference to the three research questions. (1) How does the positive cluster ion spectrum change when glyoxal is added to a ammonia-sulfuric acid system? (2) What effect does temperature hold on the positive cluster ion spectrum? (3) How does the CERN Proton Synchrotron π^+ beam influence a positive APi-ToF spectrum?

First, an introduction of the theoretical background of the mechanisms ruling the experiments will be given, followed by an elaboration on how the experiments were carried out. Lastly, the results will be discussed and some conclusions will be formulated.

2. Theoretical Background

2.1. The Atmosphere

The earth's atmosphere is an omnipresent constituent of our world. It is always there, rarely noticed and crucial for life on earth. It affects the planets temperature and shields us from harmful radiation. [19]

The term atmosphere defines a gas which surrounds a planet and that is trapped in its gravitational field [20]. One can differentiate between a planet's primary and secondary atmosphere. A primary atmosphere describes gases which have been trapped in the gravitational field while the planet was forming. It is known that earth's present atmosphere is not primary due to the lack of rare gases compared to their abundance in space. If the gases would have been captured upon the planets formation, the rare gases present in space must be present in a certain intensity. A secondary atmosphere is one which formed through volatile compounds present in the building blocks of the planet itself, escaping the solid matter and then being trapped in the gravitational field. This is the kind of atmosphere which surrounds our planet today. [21]

Over the course of earth's evolution, the atmosphere evolved as well. Volcanism and the formation of the ocean alongside many other processes have shaped the atmosphere to what it is today. 99.9% of it consists of only 3 gases. Nitrogen (N_2) makes up 78.084%, oxygen (O_2) makes up 20.946%, and argon (Ar) makes up 0.934% [22]. But these gases are not what drive the dynamic processes shaping our climate and weather. N_2 , O_2 , and Ar are very inert, meaning they rarely partake in chemical reactions. The species driving the processes taking place in our atmosphere and partaking in chemical reactions are trace gases. Trace gases, like H_2SO_4 , are all other constituents of our atmosphere apart from N_2 , O_2 , and Ar, which have characteristically low mixing ratios of below 0.1%. [21, 23]

The atmosphere can be divided into different vertical regions based on temperature as

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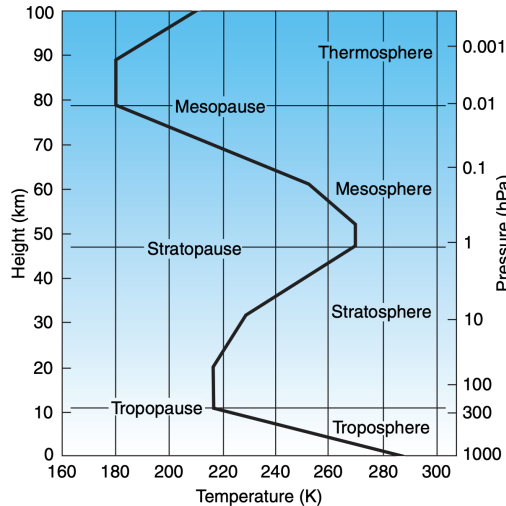


Figure 2.1.: Vertical temperature profile of the atmosphere [26].

seen in figure 2.1. As the air density decreases with altitude, the atmospheric constituents accumulate in the lower regions. Consequently, most chemical reactions take place in the troposphere and stratosphere. The troposphere is the lowest layer, where temperature decreases with increasing altitude. The boundary layer, which is considered a part of the troposphere, is the layer directly adjacent to earth's surface. Most of the time it is between 1-2 km thick, depending on local and meteorological conditions. The troposphere is the region in which weather takes place. At 10 km, a minimum temperature of around $-60\text{ }^{\circ}\text{C}$ (or 215 K) is reached, marking the transitional region to the next layer. The transitional region is called tropopause. Transitional regions are characterized by having a constant temperature profile. The subsequent layer is the stratosphere. In contrast to the troposphere, the temperature is now increasing with increasing height, reaching a maximum at around $0\text{ }^{\circ}\text{C}$ (or 270 K) and 50 km of altitude. Before the temperature decreases again with increasing altitude, there is another transitional regime called the stratopause. The remaining layers are the mesosphere, thermosphere and exosphere, which stretch to over 500 km in altitude. [24, 25, 26]

2.2. New Particle Formation

Aerosol particles are key players in our atmosphere. They can be characterized as either primary or secondary particles, as mentioned in section 1. The process which results in the formation of secondary aerosol particles in the atmosphere is called new

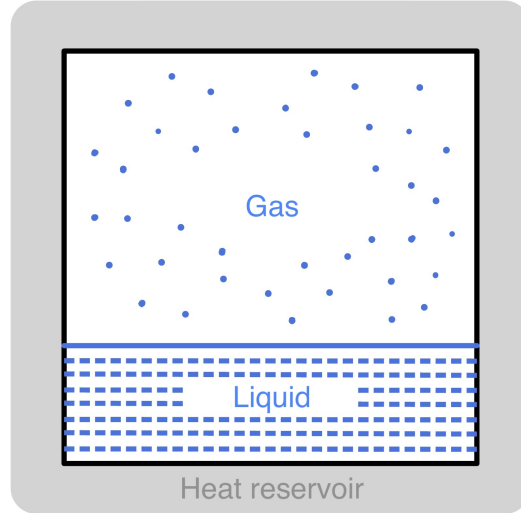


Figure 2.2.: Schematics of a closed thermodynamic system connected to a heat reservoir, after Lohmann et al. [2].

particle formation (NPF). It is initiated by the nucleation of molecules to small clusters. Nucleation can occur in four general cases. Homogeneous-homomolecular, homogeneous-heteromolecular, heterogeneous-homomolecular, and heterogeneous-heteromolecular. These classification categories reflect the state of the environment and the vapor in which nucleation occurs. A nucleation process is heterogeneous if it takes place on a foreign body, homogeneous if not. Such foreign bodies could for instance be primary aerosol particles or ions. The term homomolecular indicates that the vapor which is nucleating is a single species. Heteromolecular nucleation in contrast, occurs from a multi species vapor mixture [27]. But nucleation cannot take place spontaneously at any state of a system. It only occurs when a system is in a non equilibrium metastable thermodynamic state. [3, 28]

2.2.1. Thermodynamics of a Phase Transition

In a thermodynamic system containing two states, a phase transition takes place when the system is out of its thermodynamic equilibrium. The thermodynamic equilibrium is reached when no net macroscopic flows of energy and mass are present. This section (2.2.1) will follow the description of Lohmann et al. [2] if no other sources are indicated.

Considering a closed system which is connected to a heat bath, resulting in a constant temperature T , like seen in figure 2.2, a minimum principle for the Helmholtz free energy F can be formulated. F is the maximum amount of work a closed system can fulfill at

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constant volume and temperature.

$$F = U - TS \quad (2.1)$$

U depicts the internal energy of the system, and S its entropy. The minimum principle states that the variables on the right side will change in order to reach a minimum value of F for the systems thermodynamic equilibrium. Figuratively speaking, this leads to either condensation or evaporation in the case of a gas and a liquid phase being present. Consequently, the pressure of the system changes.

To expand this principle to atmospheric conditions, the minimum principle of the Helmholtz free energy F is no longer sufficient. This is due to the atmospheric boundary condition that the pressure stays constant. To apply this constraint to the schematics of figure 2.2, it implies that under a phase transition from vapor to liquid phase with constant T , the pressure p would not change but the volume V of the system does. The system is closed in respect to its total particle numbers N , but not in the respect to the particle numbers of each phase N_j . The minimum principle then evolves to equation 2.2, where now the Gibbs free energy G gets minimized. The Gibbs free energy is in turn the maximum work which a closed system can fulfill at constant pressure and temperature.

$$G = U - TS + pV \quad (2.2)$$

When there is a flux of mass and energy between the phases, G will change. The infinitesimal change in G can be expressed as the following:

$$dG = \sum_{j=1}^2 (dU_j - TdS_j - S_jdT + pdV_j + V_jdp) \quad (2.3)$$

The internal energy U_j can be put as

$$dU_j = TdS_j - pdV_j + \mu_j dN_j, \quad (2.4)$$

where μ_j is the Gibbs free energy per molecule in one state, also known as the chemical potential. This leads to the following expression of dG :

$$dG = \sum_{j=1}^2 \mu_j dN_j \quad (2.5)$$

As for the constraint of constant total particle number N , the change in number of each phase is directly connected as in $dN_1 = -dN_2$. This concludes the infinitesimal change of G as

$$dG = dN_1(\mu_1 - \mu_2) \quad (2.6)$$

Equation 2.6 demonstrates that the driving force of the phase transition is the difference in the chemical potentials between the two phases, $\Delta\mu$ [28]. The bigger $\Delta\mu$, the more condensation or evaporation occurs. $\Delta\mu$ can also be expressed in terms of the saturation ratio S , where k_B is the Boltzmann constant and T the temperature of the system.

$$\Delta\mu = k_B T \ln S \quad (2.7)$$

Note that the saturation ratio has the same letter accounted to it as entropy has. From now on, S will only refer to the saturation ratio, not to the entropy of a system. The saturation ratio of a system, also referred to as simply the saturation, is defined as the ratio of the present pressure in the vapor phase p_V to the saturation pressure of the species, i.e. the vapor pressure p_{sat} at equilibrium at temperature T . [28, 29]

$$S = \frac{p_V}{p_{sat}} \quad (2.8)$$

Consequently, the saturation S of a system indicates whether or not a phase transition can take place. If $S = 1$, the system is in thermodynamic equilibrium. If $S > 1$, the chemical potential of the vapor phase μ_v is bigger than the chemical potential of the liquid phase μ_l . As a system always strives towards equilibrium, it is energetically favorable to increase the number of molecules in the liquid phase at cost of the number of molecules in the vapor phase. Such a system is called supersaturated. If $S < 1$, the opposite is true and the system is undersaturated. [2, 27, 28, 29]

2.2.2. Homogeneous Nucleation

To apply the thermodynamics of a phase transition to the more specific case of nucleation, the classical nucleation theory is used. Nucleation is a phase transition of a vapor to its liquid or solid state, i.e. condensation. The description of nucleation in the following will be done for the vapor to liquid case, as this is the process of interest for the experiments carried out. As stated in section 2.2, homogeneous nucleation is the process of nucleation without a foreign body present. Hence, only the vapor molecules them-

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selves are involved in the process [27]. In order for them to form a cluster, the molecules need to collide and stick together in a sufficient amount. In this case, molecules are also referred to as monomers, indicating the singular presence of them. Consequently, a dimer is a formation of two molecules and this nomenclature continuous in this manner. Classical nucleation theory assumes a sticking probability of one. [28]

As described in section 2.2.1, the phase transition from vapor to liquid phase only takes place in a supersaturated system. But even if the system is supersaturated, condensation cannot take place spontaneously. The formation of clusters requires Gibbs free energy. This energy can be viewed as an energy barrier ΔG_i which has to be overcome for a cluster formation of i molecules. [27, 29]

$$\Delta G_i = -i\Delta\mu + A_i\sigma \quad (2.9)$$

The first term in the equation, $-i\Delta\mu$, can be interpreted as the negative bulk contribution, or the volume term. i describes the number of molecules in the cluster. The bulk contribution is the energy which the molecules are bringing with them and thus it is lowering the energy barrier. The second term, $A_i\sigma$, is the positive surface term, where A_i is the surface area of a cluster of i molecules, and σ is the surface tension. For small i , the positive surface term dominates the equation, leading to a bigger ΔG_i . This can be interpreted as the unfavorable situation of a small cluster forming for a comparably large uncompensated surface energy. For larger i , the negative bulk contribution overshadows the surface energy term, decreasing ΔG_i , making it more energetically favorable to keep adding molecules to the cluster. [28]

In figure 2.3, the work necessary for a cluster forming is visualized as a function of its radius r_i . For the two cases of $S < 1$ and $S = 1$, the energy which is needed to add one more molecule to a cluster, so to increase its radius, rises exponentially. Hence, it is always energetically favorable for a cluster to decrease its size. For the case of a supersaturated vapor, the work needed to increase the cluster size also increases at first, but reaches a maximum at r_i^* , i.e. the critical cluster size, and decreases rapidly after that. After r_i^* is reached, it is energetically favorable to further increase the clusters size. To cross the initial energy barrier ΔG_i is a stochastic and kinetic process. [28, 29]

Critical Cluster Size

Figure 2.3 visualizes the maximum of Gibbs free energy which has to be surpassed for a stable cluster to form. This maximum value of ΔG_i corresponds to the critical

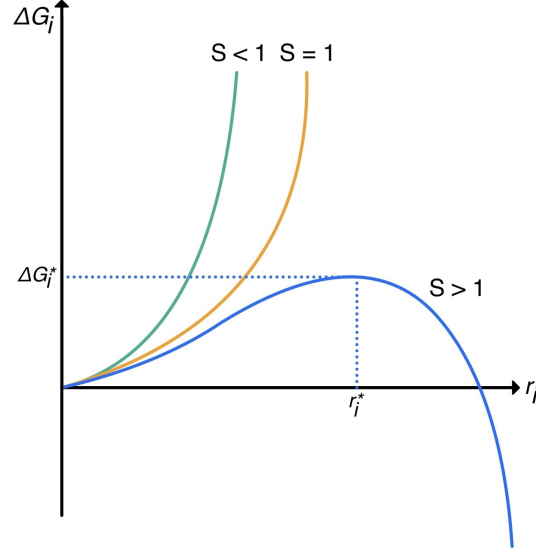


Figure 2.3.: Work for cluster formation ΔG_i against cluster size r_i . [29]

cluster size r_i^* . r_i^* describes the radius where the rate of condensation and evaporation of molecules of the cluster are equal. For bigger r_i , condensation onto the cluster dominates, for smaller r_i , evaporation does. Evaporation is independent of the saturation for a given temperature. It primarily depends on the number of molecules in the cluster, while decreasing with increasing i . The condensation-rate is proportional to S , but independent of i . Thus, with an increasing number of molecules in one cluster, the evaporation rate declines while the condensation rate stays constant, making for one cross-sectional point where both are equal.

The critical cluster size can be calculated as the partial derivative of ΔG_i to r_i which leads to the Kelvin equation [27, 28]:

$$\ln S = \frac{2\sigma}{n_l k_b T r^*} \quad (2.10)$$

The Kelvin equation relates the saturation over a spherical liquid cluster to its critical radius. n_l describes the number of liquid molecules per unit volume. Rearranging the Kelvin equation to the critical cluster size brings the following expression:

$$r^* = \frac{2\sigma}{n_l k_b T \ln S} \quad (2.11)$$

Plugging equation 2.11 into a more detailed form of ΔG_i^* , where the explicit terms for

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the surface A_i and the number of molecules i are used, leads to:

$$\begin{aligned}\Delta G_i^* &= 4\pi r^{*2}\sigma - \frac{4\pi}{3}r^{*3}n_l k_b T \ln S \\ &= \frac{4\pi\sigma}{3}r^{*2}\end{aligned}\tag{2.12}$$

Equation 2.11 states that the critical cluster size decreases with increasing supersaturation. Equation 2.12 demonstrates that the work ΔG^* necessary to form a cluster decreases with decreasing size of the critical cluster r^* . In conclusion, it can be formulated that in an environment with a higher supersaturation ratio S , the critical cluster size, which needs to be overcome for a stable particle to form, gets smaller, which also decreases the Gibbs free energy ΔG_i^* that must be available. Hence, by statistics, a higher saturation makes for an easier formation of clusters. [28, 29]

Nucleation Rate

The nucleation kinetics give light at how many particles are formed in a new particle formation event and at what rate. Under the assumption of classical nucleation theory that a molecule sticks to a cluster upon collision with a probability unity, a rate equation of cluster formation can be formulated.

The nucleation rate equation J follows a Boltzmann distribution, but kinetics have to be accounted for. This is done through the kinetic pre-factor C .

$$J = C \cdot e^{-\frac{\Delta G_i^*}{k_B T}}\tag{2.13}$$

C combines the Zeldovich factor Z , the capture rate c_i^* and the number density n_i . The Zeldovich factor accounts for differences between the vapor in its equilibrium and nucleating state and that clusters, which have already grown past the critical cluster size, can also evaporate back to subcritical sizes [29]. The capture rate describes the number of molecules hitting the surface of the cluster and the number density gives the number of gas molecules per volume. [28]

2.2.3. Heterogeneous Nucleation

Heterogeneous nucleation describes the process of nucleation on a foreign body. In the atmosphere such a body can be a pre-existing non-soluble seed particle, soluble seed

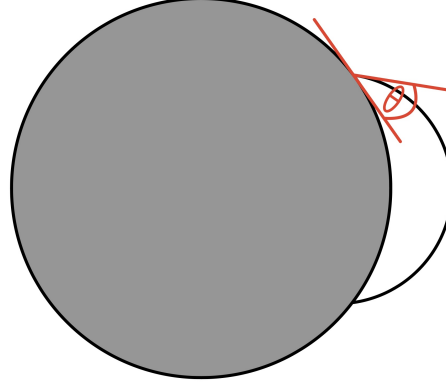


Figure 2.4.: Visualization of the contact angle θ between a seed particle and a nucleating cluster, after Kalikmanov [28].

particle or an ion [30]. The contact to a foreign body during the process decreases the energy barrier ΔG_i^* which has to be overcome for a new particle to form. The definition of ΔG_i^* gains an additional term in comparison to homogeneous nucleation (see eq. 2.9) which accounts for the contact between the nucleating cluster and the pre-existing surface.

$$\Delta G_{i,het} = -i\Delta\mu + A_{lv}\sigma_{lv} - A_{sl}\sigma_{lv}\cos(\theta) \quad (2.14)$$

A_{sl} defines the cross-sectional area between the liquid and the solid, A_{lv} the surface between the liquid and the vapor, i.e. the surface of the cluster. σ_{lv} is the surface tension between the liquid and vapor and θ is the contact angle between the newly forming cluster and the seed particle, visualized in figure 2.4.

The critical cluster size is again derived from the partial derivative of the work of cluster formation ΔG_i to the cluster size r_i . This leads to the same expression for the critical cluster size as for homogeneous nucleation, the Kelvin equation (see eq. 2.11). Inserting equation 2.11 into equation 2.14 results in an expression for the height of the energy barrier for nucleation, i.e. $\Delta G_{i,het}^*$:

$$\Delta G_{i,het}^* = \frac{4\pi\sigma_{lv}}{3}r_i^{*2} \cdot f(\cos(\theta), \frac{r_p}{r^*}) \quad (2.15)$$

The function $f(\cos(\theta), \frac{r_p}{r^*})$ is called the Fletcher factor [31]. It is a purely geometric function depending on the contact angle and the relative size between the seed particle r_p and the nucleating cluster r^* . It varies between 1 and 0. If $f = 0$ ($\theta = 0^\circ$, $\frac{r_p}{r^*} \geq 1$), the energy barrier would go to zero and a barrier-less nucleation process can occur. If $f = 1$ ($\theta = 180^\circ$, independent of $\frac{r_p}{r^*}$), the expression for $\Delta G_{i,het}^*$ becomes identical to the

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case of homogeneous nucleation. Hence, in any other case than $\theta = 180^\circ$ heterogeneous nucleation is more favorable than homogeneous. Homogeneous nucleation can be viewed as a special case of heterogeneous nucleation. [28]

Ion Induced Nucleation

Ions are a subtype of pre-existing particles on which nucleation can occur. In the atmosphere, such ions are for example the ammonium ion NH_4^+ , or the bisulfate ion HSO_4^- . The atmospheric ion will be introduced further in section 2.4.4. Ions have been found to significantly increase the nucleation rate in a system. Katz et al. [11] for example observed a 2500 fold increase in nucleation rate in the presence of an ion density of $16 \cdot 10^6$ per cm^3 . The electrostatic force field of the ion pulls in the molecules which have already condensed on the cluster. This makes the re-evaporation of them less probable. The probability of a molecule condensing onto the cluster does not change in the presence of an ion. But as the critical cluster size determines the equilibrium between condensation and evaporation from and to the cluster, the lowering of only the evaporation-rate makes this equilibrium appear at a smaller cluster size. Thus, the critical cluster size r_i^* and the Gibbs free energy are smaller. [27]

As the force field of an electric charge decreases with $1/r^2$, the effect of it is most noticeable for small clusters. Winkler et al. [30] found that the charge effect on ion induced nucleation becomes irrelevant for cluster diameters of 4 nm and bigger. Furthermore, due to the ions self repulsion and the comparatively low ion concentrations in the atmosphere, forming clusters almost exclusively only contain a singular ion. [27]

The Kelvin equation, connecting the saturation ratio to the critical cluster size, evolves for the case of ion induced nucleation to the Kelvin-Thomson equation.

$$\ln(S) = \frac{2\sigma}{n_l k_B T r^*} - \frac{q^2}{32\pi^2 \epsilon_0 n_l k_B T r^{*4}} \left(1 - \frac{1}{\epsilon_l} \right) \quad (2.16)$$

In the additional term, q ($q = i \cdot e$) describes the charging state of the ion carrying i elementary charges e . As q is squared, the reduction of the saturation ratio is not influenced by the ions sign. ϵ_0 and ϵ_l are the electrical constant and relative permittivity of the liquid, respectively. The term accounting for the electric force field reduces the saturation ratio required for a critical cluster to form. [27, 32]

The strong influence of the electric charge on small cluster ions makes for a unique behavior of the energy barrier which has to be overcome for cluster formation, as seen

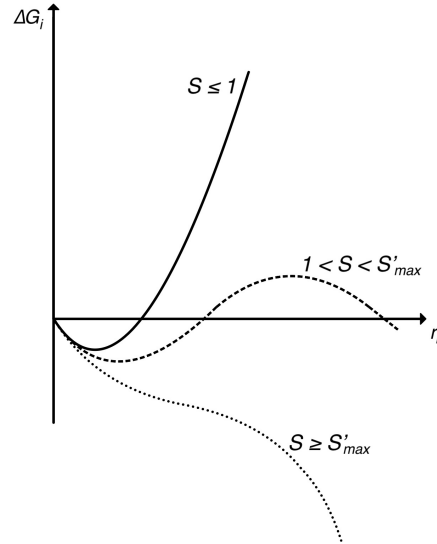


Figure 2.5.: Energy barrier for ion induced heterogeneous nucleation, based on Seinfeld and Pandis [27].

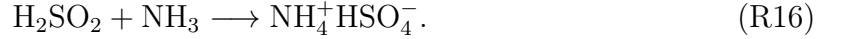
in figure 2.5. For a saturation ratio higher than S'_{max} , a barrierless nucleation process is possible, where S'_{max} is the maximum saturation ratio where no barrierless nucleation is possible. Unlike homogeneous or neutral heterogeneous nucleation, the work of cluster formation ΔG_i is negative for every saturation ratio S for the smallest of clusters, meaning that the growth is always energetically favorable in this size range. This leads to a minimum of the work of cluster formation at a stable subcritical cluster size for the cases of $S \leq 1$ and $1 < S < S'_{max}$. For the case of $1 < S < S'_{max}$ the curve of ΔG_i increases until the unstable critical cluster size r_i^* is reached. The difference of ΔG_i between the stable subcritical cluster size and the unstable critical cluster size is now the energy barrier which has to be crossed for a cluster to grow beyond its critical radius. [27, 30, 32]

2.2.4. Base-stabilization Nucleation Mechanism

The base-stabilization mechanism describes a new particle formation pathway involving acids and bases which together form more stable clusters. Acids are species which donate a proton and bases are such which take protons up. The mechanism was first described by Kirkby et al. [5], on the basis of experiments carried out at the CERN CLOUD chamber. The study analyzed the composition of nucleating clusters (with a focus on negatively charged clusters) in a system containing sulfuric acid and ammonia. The

2. Theoretical Background

main finding was that the growth of sulfuric acid molecules is suppressed for clusters with $n \geq 4$, where n is the number of molecules per cluster. When ammonia was in the chamber in high enough concentrations (in the range of pptv, depending on the systems temperature), cluster ions consisting of both sulfuric acid and ammonia could be observed, with the highest abundance for clusters of equal sulfuric acid and ammonia molecules. The size of the cluster ions was far above that of pure sulfuric acid cluster, with $n(\text{H}_2\text{SO}_4)$ (and consequently also $n(\text{NH}_3)$) as big as 20. Alongside the increase in cluster ion abundance, also the nucleation rates (J-rates) increased with ammonia present. The increase in J-rate was found to be 100-1.000 fold with atmospherically relevant ammonia mixing ratios of 100 pptv. As the name may already suggest, sulfuric acid is the acid partner in this reaction and ammonia thus the base. Together the two react to ammonium bisulfate ($\text{NH}_4^+\text{HSO}_4^-$), a reaction where H_2SO_4 donates one proton to the NH_3 molecule.



Thus, it can be formulated, that the nucleating clusters are growing by a stepwise addition of basic molecules, where each of them stabilizes one additional acidic molecule on the cluster. [5, 33, 34]

2.3. Connection to Cloud Formation

Having discussed the formation of aerosol particles in the atmosphere, the next important step is to consider their influence on cloud formation. Not all aerosol particles can grow into cloud droplets under atmospheric conditions. Whether or not a particle can grow into a cloud droplet depends on their individual composition and size. Particles which can be activated to grow into cloud droplets are so called cloud condensation nuclei (CCN). [2, 13, 27]

Köhler equation

The process of a particle being activated into a cloud droplet is described by the Köhler equation. The Köhler equation connects the necessary critical saturation ratio S_{crit} to the activation radius r_{act} of a specific type of particle. It incorporates the effect of the solution a liquid particle consists of. Having crossed the activation radius, the particle can keep growing up to the size of a cloud droplet eventually. [2, 27]

The critical saturation ratio of a particle depends on two main characteristics, radius and solubility of particle material. The radius affects the activation in a way, where the smaller the particle is, the more easily molecules can escape again as they are bound less strongly due to the high curvature. This is the same effect also observed for nucleating clusters, the Kelvin effect. On the other hand, the solubility of the particle always lowers the saturation ratio. This can be explained by Raoult's law. Raoult's law states that the vapor pressure over a solution is always lower than the saturation vapor pressure over the pure solute. Thus, solutions have a lower evaporation-rate than the pure solute in the same environment. The Köhler equation combines the two effects.

$$S = \underbrace{\frac{2\sigma}{n_l k_B T r}}_{\text{Kelvin term}} + 1 - \underbrace{\frac{3im_{sub}M_l}{4\pi M_{sub}\rho_l r^3}}_{\text{Raoult term}} \quad (2.17)$$

In this equation, m_{sub} [kg] and M_{sub} [kg/mol] describe the mass and the molar mass of the substrate dissolved in the particle, respectively. An example for a substrate is for example sodium chloride (NaCl). M_l [kg/mol] and ρ_l describe the molar mass and the density of the solute, which is water for the atmospheric case. i in this case is the Van't Hoff factor which describes the substrate's ability to dissolve into ions (e.g., $i=2$ for NaCl, Na^+ and Cl^-). [2]

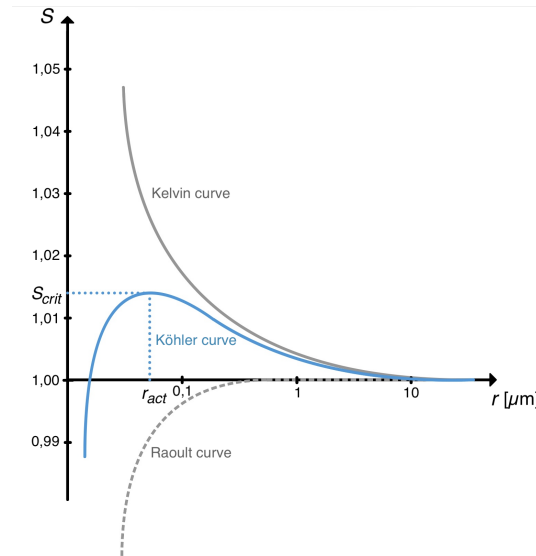


Figure 2.6.: Köhler curve, based on Lohmann et al. [2].

Figure 2.6 depicts the relationship between the saturation ratio and the radius of a potential CCN. Generally, the curve in figure 2.6 relates the different sizes of a growing

2. Theoretical Background

particle to their respective equilibrium saturation ratios. That is to say, that at saturation ratio x , the a particle can grow up until the size r_x . S_{crit} is the saturation ratio which is needed in order for this particle to grow into a cloud droplet. The corresponding size of that droplet which has to be exceeded is the activation radius r_{act} . Once the size of r_{act} has been crossed, the particle will grow further as long as $S > 1$. S_{crit} , and hence shape of the Köhler curve, differs for varying particle materials. Observable from figure 2.6 is that only through the addition of the substrate, leading to a Raoult term, the saturation ratio of respective sizes is low enough for particles to grow. [2, 35]

2.4. Chemistry of the Atmosphere

The following section discussing the atmospheric chemistry is based on the book of Seinfeld and Pandis [27], if not indicated otherwise.

In the preceding description of NPF, it becomes evident that chemistry plays a significant role in the process. Chemical reactions taking place in our atmosphere are mainly three different reaction types. These are the first-, second-, and third-order reactions, as seen in the reaction equations R1, R2, and R3.



The first reaction describes the process of decomposition of one singular molecule, also called uni-molecular reaction. No reaction partners are needed for this reaction. This can be spontaneous radioactive decay or decomposition through photo-dissociation. The latter will be discussed in more detail in the subsequent paragraph. R2 describes a chemical reaction of two reaction partners which form two daughter compounds upon reaction. R3 displays a reaction where a third reaction partner takes up excess energy to stabilize the excited intermediate reaction product AB^* . The third body does not undergo chemical alteration but only a change in energy.

The most important class of uni-molecular reactions in the atmosphere are photolysis reactions. These are such where the incoming energy from the sun $h\nu$ provides the energy

needed for the molecule to split up. Such photo-dissociation reactions are written as:



The rate at which a reaction occurs is given by the change in number concentration of the mother-molecule A over time. It displays how many reactions take place in one cubic centimeter per second [$1/\text{cm}^3\text{s}$].

$$\frac{dA}{dt} = -kA \quad (2.18)$$

k is the rate coefficient, a proportionality constant relating the molar concentration of A to the reaction rate $\frac{dA}{dt}$. It is given in reciprocal seconds [$1/\text{s}$]. Integrating equation 2.18 results in an expression for how many molecules of A are present at anytime, when knowing the initial concentration A_0 .

$$A(t) = A_0 e^{-kt} \quad (2.19)$$

Trace Gases

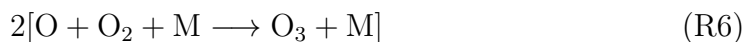
As mentioned in section 2.1, the constituents which drive atmospheric chemistry are the trace gases. They can undergo chemical reactions and also absorb electromagnetic radiation coming from the sun or the earth. The absorption is the characteristic which makes a trace gas a green house gas. While earth's atmosphere is mostly transparent for the incoming solar shortwave radiation, the outgoing terrestrial longwave radiation can be absorbed more efficiently by the green house gases. The increase of trace gases leads to an increase in absorbed terrestrial radiation, resulting in an increase in earth's radiation budget. The consequence of this is an increase in global mean surface temperature.

CO_2 is arguably the most well known trace gas connected to climate change. This is for good reason, as the gas is not only emitted in extreme amounts by human activities, but it also absorbs longwave radiation $\geq 10 \mu\text{m}$ with an efficiency of almost 100%, making it one of the most potent greenhouse gases known. Other important trace gases, especially for the process of new particle formation, are ozone (O_3), the hydroxyl radical ($\text{OH}\bullet$), sulfuric acid (H_2SO_4), and ammonia (NH_3). An introduction of them will be given in the next chapters. This will underline how important the atmospheric chemistry is for NPF once more, as the majority of precursor gases are not emitted directly into the atmosphere, but must first be formed chemically. [5, 36]

2.4.1. O₃ and OH Chemistry

Ozone is highly reactive and plays a role in many chemical reactions but is also a crucial component of the atmosphere on its own as it absorbs ultra-violet (UV) radiation. Around 97% of the harmful UV radiation with $\lambda < 310$ nm is absorbed by stratospheric O₃. Simultaneously, tropospheric O₃ is a strong green house gas, contributing to global warming [37, 38]. Alongside these characteristics, O₃ is also a powerful oxidant. Oxidation is a process where one component loses an electron, which oftentimes means that it loses a hydrogen atom. The oxidant is the species which oxidizes the target. The opposite process is called reduction. This describes the process where a component takes up an electron. An oxidant itself is being reduced in an oxidation event [33]. Oxidation is a very important process for the atmosphere. This process is responsible for breaking down and removing many trace and green house gases from the atmosphere. The most important oxidant of our atmosphere is OH•. But as the atmospheric cycle of OH is closely intertwined with that of O₃, the following shall discuss the production and destruction pathway of both. [39]

The only production pathway of ozone is:



This cycle takes place in the stratosphere. O₂ undergoes photolysis and the products then recombine with other O₂ molecules. It makes for a net production of 2O₃ molecules from 3O₂ molecules. This production is part of the Chapman cycle, a cycle which describes production and destruction of ozone.

The O₃ destruction pathway of the Chapman cycle is also a photolysis reaction. O₃ is either split up into O(¹D) + O₂ with UV radiation of $\lambda < 320$ nm or into O(³P) + O₂ with radiation of $400 \leq \lambda \leq 600$ nm. The more energetic UV radiation leads to a production of a single oxygen atom in an excited state, O(¹D). This atom first has to give away its excess energy to a third body before it then also reaches the O(³P) state. The O(³P) can then react with O₃ in a second order reaction to create 2O₂.

But the destruction of O₃ through the Chapman cycle does not account for all destruction of O₃ that occurs in the atmosphere. Another major O₃ destruction pathway is the so-called catalytic ozone destruction pathway. The catalytic nature of the process

results in the radical which destroys the O_3 to be conserved. This destruction takes place in the upper stratosphere. An exemplary catalytic destruction with the $OH\bullet$ radical is the following:



This makes for a net destruction of one O_3 and one O molecule while producing two O_2 molecules. The concentration of the OH radicals is not altered through these reactions. Note that the same destruction pathway can be carried out with other radicals as well.

$OH\bullet$ is not only involved in O_3 destruction, but the dependence of the two species also goes the other way around as O_3 is needed for $OH\bullet$ production. The production pathway of the hydroxyl radical is the following:



The more water vapor and ozone are available, the more $OH\bullet$ gets produced. This process can take place in both the stratosphere and troposphere. The ozone which is produced in the stratosphere can settle down to the troposphere and is then used for these reactions. Note that all photolysis reactions have daily and yearly cycles, as they depend on the presence and intensity of the solar radiation.

The destruction pathways of the hydroxyl radical are many, as $OH\bullet$ readily partakes in chemical reactions, most important in oxidation. The oxidation of carbon monoxide (CO) is shown in the following as an exemplary reaction.

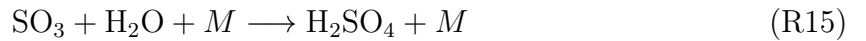


2.4.2. Sulfuric Acid

Sulfuric acid (H_2SO_4) is an important component of our atmosphere considering aerosols and new particle formation [13]. The stratospheric aerosol for example mainly consists of H_2SO_4 . But it also plays a crucial role in the troposphere. H_2SO_4 is not injected directly into the atmosphere but formed through precursor gases. Such precursor gases can be of natural or anthropogenic origin. The direct precursor gas is sulfur dioxide (SO_2). Naturally, this gas is emitted through volcanic eruptions, anthropogenically it is emitted primarily through combustion of sulfur containing coal and oil. As volcanic eruptions can transport gases up into the stratosphere, SO_2 and also H_2SO_4 are present there. The anthropogenic emission of SO_2 makes highly industrialized regions have high sulfur dioxide, and subsequently higher aerosol particle concentrations, if no regulation for emissions are in place. [19]

But in addition to directly emitted SO_2 , sulfur containing gases like carbonyl sulfide (OCS) or dimethyl sulfide (DMS) can get photolyzed and oxidized to SO_2 . DMS is emitted from the ocean, OCS from several different surfaces as well as from biomass burning. As OCS is very inert, its life time is long enough for it to enter the stratosphere, making it another source of SO_2 there.

To form sulfuric acid out of sulfur dioxide, sulfur dioxide has to get oxidized by $\text{OH}\bullet$. The production pathway of H_2SO_4 in the gas phase is the following:



2.4.3. Ammonia

Ammonia is the nitrogen containing compound NH_3 and the most important basic gas of the atmosphere. N_2 is the most abundant constituent of our atmosphere but its strong triple bond makes it highly unreactive. For it to engage in chemical reactions, it must be so-called "fixed". Fixation of N_2 refers to a process where the compound is chemically converted to any other nitrogen containing compound, which enables it to

undergo further chemical reactions. Naturally, the fixation comes about through a few microorganisms which are able to break down N_2 to ammonia, ammonium ion (NH_4^+), or organic nitrogen compounds, and also through strong ionization events on N_2 like lightning or cosmic radiation. In addition to ammonia, also the ammonium ion NH_4^+ plays a important role in new particle formation, which will be discussed further in section 4.1.

The anthropogenic impact on global NH_3 emissions has increased immensely over the last century. This is most importantly due to the production and use of synthetic fertilizers. The Haber-Bosch process is the process which allows imitation of the fixation of N_2 to NH_3 from microorganisms on an industrial scale. As this enables the production of highly efficient synthetic fertilizers, it also enables to sustain enough food for the rapidly rising population of the earth. Studies state that nowadays up to 80% of NH_3 emissions are of anthropogenic sources. [40]

2.4.4. Ions of the Atmosphere

Alongside the trace gases, ions are a fundamental part of our atmosphere. They can partake in the process of new particle formation (see section 2.2.3) where they play a crucial role. [11, 12, 41]

The primary source of ions in our atmosphere are cosmic rays. These are charged particles coming from space with energies from 1 to $5 \cdot 10^{13}$ MeV. But only those above 1000 MeV are of interest for ion formation in the atmosphere, as others have too little energy to induce ionization processes, like spallation. These processes are most important in altitudes between 3-50 km. In higher altitudes, photoionization dominates [13, 24, 42].

In the stratosphere and troposphere, the most important positive ions are the proton hydrate $H_3O^+(H_2O)_n$, with n ranging from 1-3. They are formed by a reaction channel involving H_2O and O_2^+ , or alternatively H_2O and NO^+ . The proton hydrates can be understood as the starting point of positive ion chemistry in the troposphere and stratosphere. For the positive ion chemistry, the most important reaction is the proton transfer reaction. Based on this, other ion species can form. [24]

2.5. Asian Tropopause Aerosol Layer

As indicated in section 2.1, the atmosphere is not homogeneous as a whole. Different altitudes for example have different temperatures, densities, and compositions. But the variations are not only due to difference in altitude. Also seasonal cycles, anthropogenic activities or volcanism can influence the state of the atmosphere. [19, 21, 23, 24]

CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation) measurements from 2006 to 2009 have indicated the existence of an aerosol layer which stretches from western China to the eastern Mediterranean. It was found at an altitude between 13 and 18 km [15, 16]. The layer is formed by convective lifting of pollutants, aerosols and precursor gases from the boundary layer to the upper troposphere lower stratosphere region by the Asian summer monsoon [16, 43]. Figure 2.7 shows the CALIPSO measurements, demonstrating the increased aerosol concentration in the region. The arrows giving the wind fields show that the aerosol is trapped in the anticyclone circulation. The measurement data from 2009 differs due to a volcanic eruption in Russia in June that year which led to the injection of 1 Tg of SO_2 into the stratosphere.

Yu et al. [16] present results of model calculations that conclude a composition of 60% organics (by mass) and 40% sulfate (by mass) for the Asian tropopause aerosol layer (ATAL). Further modeling studies indicated enhancements of CO and NH_3 in the ATAL due to effective convective transport. SO_2 however does not show this behavior, possibly even the opposite [44]. This could mean that also H_2SO_4 is decreased to some extent, relative to the adjacent tropopause. As the emissions in central and east Asia are only increasing, the effect of the ATAL is predicted to intensify. Particles and trace gases contained in it can travel to other regions, which globalizes the effect of increased stratospheric aerosols [45].

Glyoxal in the ATAL

After the discovery of the ATAL, it is now of interest how new particles can form within it, to contribute to the enhanced particle concentrations.

Glyoxal ($\text{C}_2\text{H}_2\text{O}_2$) is an oxidation product of volatile organic compounds (VOCs). More precisely, it is formed, when hydrocarbons of 2 or more carbon atoms get oxidized. It has natural and anthropogenic sources, such as biogenic VOCs that are emitted by trees or acetylene (C_2H_2), which is a compound emitted by industry. As Asia is a hot spot for industry and also has a significant amount of forests, glyoxal concentrations in

2.5. Asian Tropopause Aerosol Layer

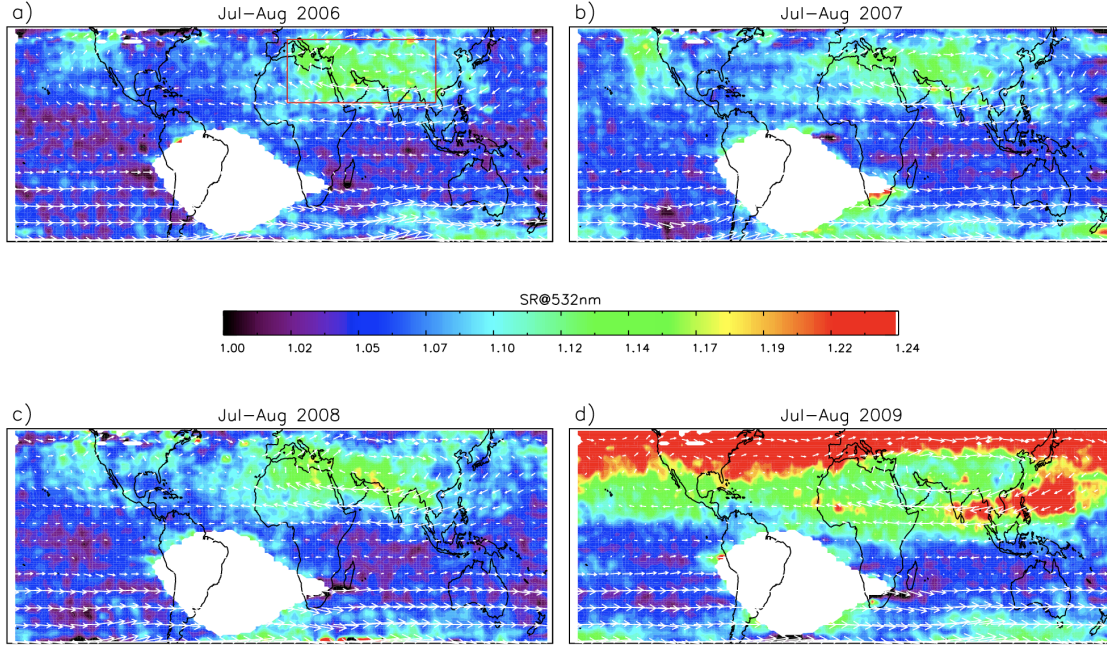


Figure 2.7.: Asian tropopause aerosol layer from CALIPSO measurement data. The map displays the scattering ratio (SR) of 532 nm between 15 and 17 km altitude, where the SR is a measure of how much more light is back-scattered compared to clean air [46]. The white arrows indicate wind fields. Measurements from 2009 show a different behavior due to a volcanic eruption and subsequent injection of SO₂ in the tropopause/stratosphere. [15]

this region are enhanced. As one of the main sinks of glyoxal is aerosol uptake [18], it is of interest to study how it affects new particle formation. This can be best done with quantitative experiments under well-controlled chamber conditions. [15, 16, 47]

3. Material and Methods

3.1. The CERN CLOUD Experiment

The CERN CLOUD (Cosmic Leaving OUtdoor Droplets) experiment is a state-of-the-art experiment which studies the microphysics of atmospheric new particle formation events. The center piece of the experiment is a 26,3 m³ stainless steel chamber (also called the "CLOUD chamber"). Inside the chamber, gas mixtures resembling specific atmospheric conditions can be recreated and analyzed for various parameters. Having an ultra clean environment is extremely important for the measurements, as the concentrations of certain trace gases which can induce nucleation in the atmosphere can be as low as a few parts-per-trillion by volume (pptv). To recreate such pristine systems, the chamber is connected to a gas system which can supply the necessary trace gases through individual lines and ports. The gas system also supplies ultra-pure synthetic air to the chamber. The synthetic air is made up of a 79:21 ratio of N₂ and O₂. To further control the processes happening in the chamber, the temperature can be set anywhere from -60 to 100°C, although the extremely high temperatures are rather used for a cleaning of the chamber than to simulate atmospheric conditions. The chamber is additionally equipped with an insulating thermal housing, which makes the chamber temperature independent of outside conditions. The chamber is equipped with a light system made up of several different lamps in order to simulate different radiation conditions and allow for photo-chemical reactions. A fiber-optic UV system operating in a range from 250-400 nm is located at the ceiling of the CLOUD chamber. Additionally several light sabers operating at wavelengths between 251 and 528 nm are placed on the chamber walls. Also on both the bottom and the top of the chambers, stainless steel fans are mounted in order to remove ions within seconds and provide conditions for neutral nucleation. Furthermore, these fans can be used to ensure a homogeneous mixing of the gases and particles. The standard operating pressure in the chamber is +5 mbar relative to atmospheric pressure, but this can be increased to +200 mbar relative to atmospheric pressure if needed for

3. Material and Methods

the experiment. To investigate one of CLOUDs main research questions, which is how galactic cosmic rays influence new particle formation events in the atmosphere, the chamber can be exposed to a 3,5 GeV/c secondary π^+ beam from the CERN Proton Synchrotron. This recreates the ion concentrations at the top of the troposphere, with ion pair concentrations of around 3000 $1/\text{cm}^3$. To simulate neutral conditions, electrodes inside the chamber can be turned on, which leads to removal of ions. These electrodes are mounted on the bottom and top of the chamber and can apply an electric field of up to 30 kV. The third ionization state which can be explored in the chamber is representative of galactic cosmic rays (GCR) in the boundary layer. This state is achieved by neither running the π^+ beam nor the electric field, corresponding to ambient conditions. Here, the ion pair concentration is around 400 $1/\text{cm}^3$. To carefully observe what is happening in the chamber, 16 sampling ports are built in. To each sampling port, at least one measurement instrument can be connected. The instruments can be organized into three main categories. Mass spectrometers, particle counters/sizers, and gas phase analyzers. Together they provide a detailed look into what the conditions in the chamber are. In the so-called control room, the live data collected by these instruments is monitored. An exemplary picture of the CLOUD experiment can be found in figure 3.1. [12, 48]

3.1.1. Glyoxal Experiment at CLOUD17

The experiments exploring the role of glyoxal in the Asian tropopause aerosol layer (ATAL) were carried out over the course of 8 days during the CLOUD17 campaign in the fall of 2024. Due to a build up of background contaminants of unwanted species from the previous experiment, the first day was used to clean the chamber thoroughly. This makes for 7 days of the experiment.

Half of the 7 experimental days were held at -30°C and half at -50°C chamber temperature. In the -30°C environment a relative humidity (RH) of 60% was applied, and in the -50°C environment a RH of 100% was applied. In both of those environments, various compositions of a sulfuric acid + ammonia + glyoxal system were explored, meaning that the individual concentrations of the components were varied. Additionally, background measurements of a pure sulfuric acid system as well as a sulfuric acid and glyoxal system were held at the beginning of the experiments. The mixing of the chamber air was held constant at a fan intensity of 12% throughout all experiments. The experiments were carried out under cosmic ray ion intensities, representative of boundary layer conditions, and under influence of the secondary π^+ beam, which is representative of the conditions

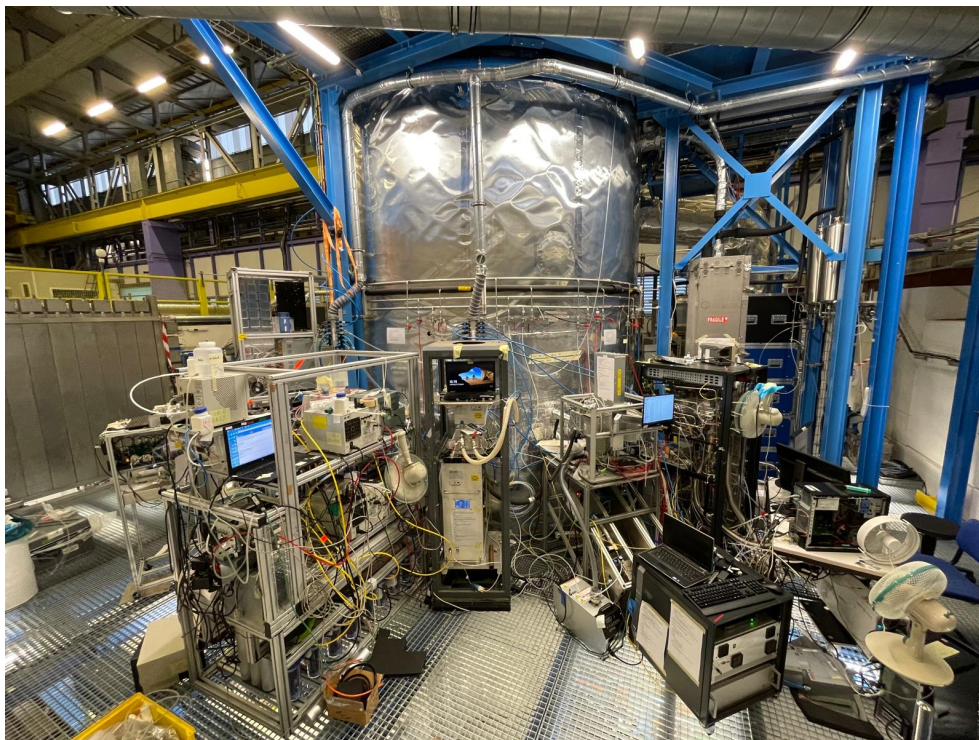


Figure 3.1.: CLOUD chamber during the CLOUD17 campaign in the fall of 2024, self taken.

at the top of the troposphere. The light conditions in the chamber were held constant with two light sabers emitting at 251 nm turned on at all times.

Glyoxal and ammonia can directly be injected to the chamber. In contrast, sulfuric acid is not injected directly, but formed inside the chamber through oxidation of sulfur dioxide (SO_2) with OH. Also OH cannot be injected directly, but needs to be produced inside the chamber as well. This happens through the reaction of water vapor with $\text{O}(^1D)$, which again is produced by photolysis of ozone (O_3). The production pathway of OH is described in section 2.4.1. The OH which is produced can then partake in a oxidation reaction with SO_2 to form H_2SO_4 . The details of this reaction can be found in section 2.4.2. [49]

Consequently, the parameters which are adjusted to create different sulfuric acid concentrations in the chamber are those of SO_2 and O_3 . In table A.1 in the appendix, the concentration of the gases and other settings for the corresponding experimental runs of interest for this thesis are listed.

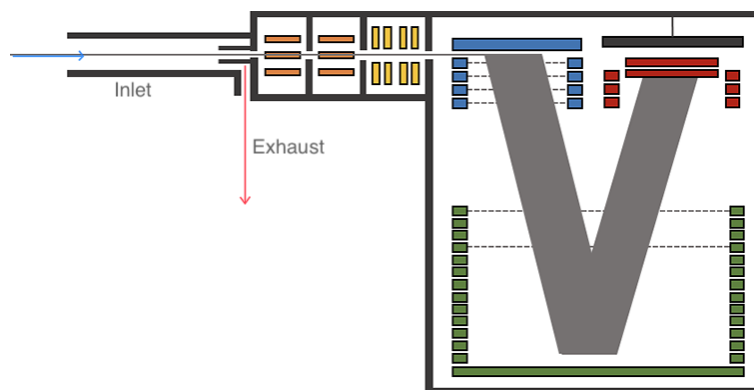


Figure 3.2.: Schematics of the ioniAPi-ToF. The orange part depicts the hexapoles, the yellow part the ionoptics. The blue, red and green parts make up the time-of-flight region with blue being the extraction region, green being a reflectron and red being the detection and post acceleration region where also the MCP is located. Figure from Leiminger et al. [50] (adapted).

3.2. IoniAPi-ToF

The centerpiece of the experiments analysed for this thesis is the ioniAPi-ToF MS, which is short for Atmospheric Pressure interface Time of Flight Mass Spectrometer. The term "ioni" refers to the company which built the instrument, Ionicon.

The APi-ToF is an instrument which can measure the mass to charge ratio of ion clusters. It can either be run in positive mode or in negative mode. The different modes refer to the charge of the ions which are measured. For the experiments which were conducted, the instrument ran in the positive mode only. The schematics of the instrument can be seen in figure 3.2. The instrument is described by Leiminger et al. [50] and the following sections will be based on their work.

Starting at the top of the instrument, the inlet flow can be set between 1 to 15 liters per minute (lpm). For the CLOUD17 campaign, it was set to 10 lpm. As indicated in figure 3.2, the inlet contains a core sampling section. The sample flow which is collected through the core sampling has a flow rate of 1.1 lpm, the rest of the initial flow is guided towards an exhaust.

The instrument contains two parts, broadly speaking. The atmospheric pressure interface makes up the first part. In this region, the ions are focused and guided towards the mass spectrometer region. Within three steps, the atmospheric pressure, at which the ions are sampled, is reduced from 2.3 mbar over 10^{-3} mbar to 10^{-4} mbar. In the second part of the instrument, the time of flight region, the pressure will be further

reduced to $\sim 6\text{-}7\cdot 10^{-6}$ mbar. The initial pressure of 2.3 mbar is produced by a Pfeiffer Vacuum ACP 40 roots pump. The succeeding pressures are achieved by three Pfeiffer Vacuum HiPace 80 turbo-molecular pumps.

3.2.1. Ion Guides

After the core sampling, the ions are in the atmospheric pressure interface region. As mentioned above, this region reduces the pressure down to 10^{-4} mbar. Alongside the pressure reduction, the ions are focused into one beam and guided towards the ToF region. This is done by the ion guides.

The ion guide is composed of three parts. Two hexapols and one ion transfer optical lens system. Each part is located in one pressure stage and divided by a skimmer with a bore diameter of 1.2 mm. Radio frequencies are applied to the hexapols resulting in a collimated ion beam. The frequency of the first hexapole was set to 1 MHz and the amplitude to 10.2 V. For the second hexapole the values were 6 MHz and 10.2 V. The optical lens system focuses the ions to the extraction region for the time of flight measurement, which lies orthogonal to the incoming ion beam. It is composed of eight lenses, each with an individual voltage applied to it.

The voltages and frequencies which are applied can be adjusted in the IoniTOF software. Changing the individual settings can be utilized to tune the instrument. The tuning influences the mass to charge range of ions which is transferred most efficiently to the ToF region. [51, 52]

3.2.2. Mass Spectrometer

Directly adjacent to the ion guide is the time-of-flight region. As the name of the instrument states, it is a time of flight mass spectrometer. This means that the mass of the ions is determined via their individual flight times through a well characterized time of flight region. Since ions with different mass to charge ratios have different inertia, their flight time for the same route will be different. To determine the flight time of an ion, a start and a stop signal is needed. The start signal is achieved in the extraction region. There, the ions are pulsed away onto their flight path in bundles. The pulses make for the start signal and can be varied to different frequencies. The flight path is not straight but in a V-shape for the IoniAPi-ToF. This shape includes a reflectron

3. Material and Methods

acting like a mirror for the ions, which brings the advantage of higher mass to charge resolution. The reflectron is composed of several electrodes of steady rising voltages when approaching the back wall of the chamber. When entering this region, the ions are being slowed down and eventually accelerated in the opposite direction again. Looking at two ions of the same mass to charge ratio but different masses, the one with the higher kinetic energy will penetrate the voltage field deeper than the one with the lower kinetic energy. Thus, the ion with the higher kinetic energy will have a longer flight path inside the reflectron region, but at a higher velocity. This results in the two ions hitting the detection region at the same time. The elonged flight length and thus flight time caused by the V-shape enhances the resolution of the instrument, as longer flight times lead to more pronounced separations between the stop signals of different mass to charge ratios. The last component of the time of flight region is the detection region. Here, the stop signal of the ions is created. The signal is obtained by a multi-channel plate (MCP) detector, which enhances the charge it receives by creating an electron avalanche from the incoming charge. The instrument gathers all signals it receives within a certain small time frame and bundles them up into one so-called time bin. The number of time bins depends on the extraction frequency. For a frequency of 30 kHz, about 280 000 time bins are created. Each time bin then corresponds to one mass to charge ratio. Thus, the instrument delivers a spectra of intensity vs. mass to charge ratio per time bin. [50, 51]

3.2.3. Resolution

The resolution R the instrument delivers for the mass to charge ratios is based on the full width half maximum (FWHM) of the individual peaks. Thus, each peak has its own resolution.

$$R(m/z) = \frac{m/z}{FWHM} \quad (3.1)$$

A general trend of R for time of flight mass spectrometers is that resolution increases for higher masses. This is due to the longer flight times of heavier ions (i.e. higher m/z), which leads to better separation of the signals. The resolution of the APi-ToF ranged from 1300-2000. Compared to other instruments, the resolution is somewhat lower, which is due to the different focus of the instruments. The ioniAPi-ToF puts an emphasis on fast switching of polarities. Others focus more on higher resolution. [50, 51, 53]

3.3. Calibration of the APi-ToF

In order to accurately interpret the data collected with the APi-ToF, two characteristics of the instrument needed to be calibrated. One is the transmission efficiency η which needs to be determined, the second is the calibration of the mass axis.

3.3.1. Transmission Efficiency Measurement

The transmission efficiency is a value which gives the ratio of ions that are detected by the APi-ToF compared to the total number of ions in the aerosol. The loss of the ions occurs due to several reasons. The first one is that the sample flow, which is actually fed through the instruments measurement region, is only a small part of the flow that is sucked in at the inlet. At the core sampling, 1.1 lpm are extracted to be measured in the time of flight region of the instrument. A second reason are the hexapols. Since the voltage and frequency which is applied to the hexapols determines the masses which can pass through, they also filter out a part of the ions, decreasing the total amount of ions to be detected. Also ions which deviate from the ideal beam path due to unfavorable initial positioning are at risk to get filtered out wrongfully by the hexapols. The instrument's transmission efficiency was determined after the campaign, in Vienna. [51, 52, 54]

Experimental Setup

In order to calculate η , a second instrument for a reference measurement is required. For this, a Faraday Cup Electrometer (FCE) is used. It measures the electric current generated by the ions in the airstream, which is then translated to the ion concentration per cubic centimeter. A symmetrical experimental setup is required to ensure that both instruments are measuring the same aerosol, making the measurements comparable. The experimental setup can be seen in figure 3.3.

The experimental set up starts with the 15 lpm of pressurized air flowing through a HEPA filter. The filtered air is then directed into an electro spray generator (ESI), where ionized salt clusters are being introduced to the aerosol. Afterwards, a Vienna type high resolution differential mobility analyzer (UDMA) generates a monodisperse aerosol of the monomer or wanted polymer [55]. After the UDMA, the flow is split. First, an overflow line is installed. During normal operation, this line should extract 5 lpm. The remaining 10 lpm are divided equally in a y-splitter. Q_{ToF} is the flow which leads to

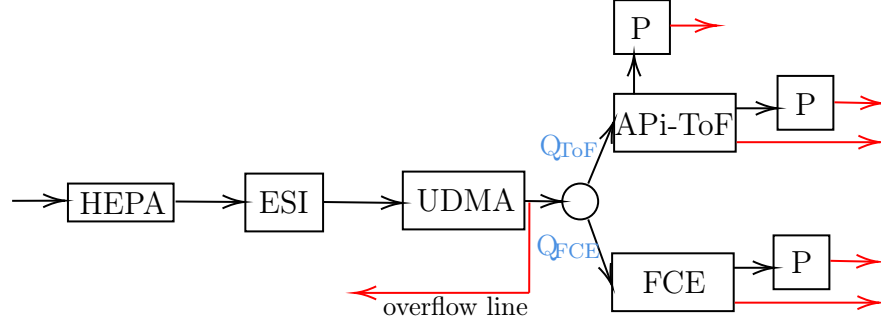


Figure 3.3.: Experimental setup for calibration and transmission efficiency measurement, after Leiminger et al. [50].

the APi-ToF, and Q_{FCE} the respective one going towards the FCE. Both are set to 5 lpm. The red arrows in figure 3.3 indicate the exhaust lines. P indicates where pumps are connected. The APi-ToF is connected to two pumps. One vacuum pump, which establishes the vacuum inside the instrument, and one inlet pump, which is responsible for the inlet flow. In addition to the two pumps, the APi-ToF is also directly connected to an exhaust. This is used to dispose the excess of the core sampling flow. [50, 56, 55]

Transmission Efficiency

With respect to the parallel measurement between the APi-ToF and the FCE, the transmission efficiency η can be defined as shown in equation 3.2. [50]

$$\eta = \frac{\text{signal}_{\text{ToF}}}{\text{ions}_{\text{FCE}}} \cdot \frac{1}{Q_{\text{ToF}}} \quad (3.2)$$

$$\text{ions}_{\text{FCE}} = \frac{I_{\text{FCE}}}{e_0 \cdot Q_{\text{FCE}}} \quad (3.3)$$

The signal that the APi-ToF returns ($\text{signal}_{\text{ToF}}$) are ion counts per second. They can be read out for each individual mass to charge ratio. The value ions_{FCE} gives the ions per cubic centimeter measured by the FCE, and can be calculated as shown in equation 3.3. Here, I_{FCE} is the electric current measured by the FCE, Q_{FCE} the flow rate of the instrument and e_0 is the elementary charge. Q_{ToF} refers to the flow rate which is measured at the inlet of the APi-ToF, not to be confused with the flow rate of the sample flow inside the instrument, which is lower due to the core sampling. As the transmission efficiency of the instrument can differ for different mass to charge ratios, different particle sizes are analyzed. For the measurement the salt tetra-heptyl

ammonium bromide (THABr) is used. The positive monomer, dimer and trimer of the salt are each examined to calculate their transmission efficiency. Their masses range from 410.47 amu to 1389.25 amu. The charging state of the salt clusters is known to be 1, thus, their mass to charge ratio measured by the APi-ToF can be recognized as their mass. [56]

The measurement spectrum for the monomer is more distinct as those for the dimer and trimer. The dimer and trimer spectra show unwanted peaks of smaller clusters, i.e. the dimer also has a monomer peak and the trimer has a dimer and monomer peak. This is possibly due to fragmentation of the dimer and trimer in the APi-ToF. Those peaks have to be accounted for while calculating their transmission efficiencies. The obtained transmission efficiencies can be found in table 3.1. [50, 54] The highest

410.47 amu (monomer)	899.86 amu (dimer)	1389.25 amu (trimer)
$(0.123 \pm 0.002) \%$	$(0.078 \pm 0.001) \%$	$(0.0050 \pm 0.0001) \%$

Table 3.1.: Transmission efficiencies, positive APi-ToF.

transmission efficiency is found for the mass of 410.47 amu. For the two higher masses, the transmission efficiency decreases. Comparing the values to literature ([50, 51, 54, 57]) suggests that the transmission efficiency ranks at the lower end, but lies in the same order of magnitude. In the compared literature, the highest transmission efficiencies achieved for comparable instruments are around 1%. It is to be noted, that a more detailed tuning of the instrument has been carried out on site of the CLOUD experiment. Thus it can be assumed that the transmission efficiency during the campaign reached higher values.

3.3.2. Mass Calibration

For the calibration of the mass axis, the two salts tetra-heptyl-ammonium-bromide (THABr) and tetra-butyl-ammonium-iodine (TBAI) were used, separately. As for the experimental setup, the same as for the transmission efficiency measurement was used, which can be seen in figure 3.3. Together, the ESI and the UDMA produce a well defined aerosol, which contains only the ion clusters of the salt. Hence, the peaks which appear in the spectrum of the APi-ToF can be matched reliably to one specific species.

For calibration of the mass axis, one assigns each time bin to a corresponding known mass to charge ratio. The mass axis can be calibrated with up to 6 points. It is beneficial

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to use clusters with a wide mass to charge range, to have coherent calibration over the whole axis. As mentioned in the last section, the charge state of the calibration clusters was known, thus, through their known masses, their exact mass-to-charge ratios were also known and could be used for calibration [56]. The mass calibration was repeated numerous times to gain information on how the instrument response changes over time.

Ideally, another mass calibration would be carried out directly before and after the experiments take place. This was not possible for the CLOUD experiment. During the experiment, the mass calibration could only be checked for known species which were in the chamber, like for the proton hydrates. This always showed alignment which indicates sufficiently good mass calibration. In addition, a mass calibration can be carried out after the data collection. Here, species of which the exact mass to charge ratio is known have to be present in the spectrum. If this is not the case, no post mass calibration is possible. This was also the case for the vast majority of the recorded spectra during the study.

4. Data Evaluation

After the experiments, the collected raw data have to be evaluated. The processing of the data involves the assessment of its quality and its analysis from a scientific perspective.

For the API-ToF, the raw data is collected with the *ioniTOF* 4.0.96 software. For the post processing of the data, the *PTR-MS Viewer* 3.4.6 software is used. Both softwares are from the company *Ionicon*. Further analysis is done with python scripts.

The post processing of the data in the *PTR MS Viewer* software involves four general steps. The first step is to cut the files into the time frames of interest. After the data frames are cut new average spectra are calculated based on the defined time frames. The new files can undergo a second (post measurement) mass calibration. Furthermore, the best fitting peak function is selected and applied to the spectrum. Lastly, a peak list can be implemented.

A peak list (or peak table) contains chemical compounds paired with their exact masses. Such peak lists can either be imported or created in the software itself. When creating or applying a peak list for or to a spectrum, a threshold of intensity is defined. All masses with peaks of higher intensities than the threshold are filtered out and added to a table, forming the individual peak list of that data frame. Imported peak lists filter out all peaks which match the imported species/masses as well as surpassing the threshold intensity. When creating a peak list inside the software, all peaks over a certain threshold are selected. Those can then be identified by hand. The threshold has to be set for each file individually, as the background levels differs due to the unique measurement times and conditions. No peak list fitting for the analyzed atmospheric systems was available, hence the peak list used for the data analysis was created during the post processing.

To create a peak list, the identifier of the *PTR-MS Viewer* software can be used. Each peak which has been recognized to be over the threshold can be analyzed and assigned with a chemical compound. Good mass calibration is crucial for the differentiation

between chemical compounds with the same nominal mass, and therefore for the peak identification process.

4.1. Peak Identification

For the peak identification process, the composition of the gas to be analyzed must be known, as these are the components which can be present in a cluster ion. How and why certain cluster ions form is a deeply chemical and physical process, and is in parts described in section 2.4 and 2.2. This section shall elaborate the more specific case of the peak identification process throughout this study.

As mentioned in section 2.4.4, the proton hydrates ($\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$) are the most important ions of the troposphere and stratosphere. Thus, they are also important markers which are always looked for in the positive ion spectrum. The range of n is 1-3, making their exact masses 37.028 amu, 55.039 amu, and 73.050 amu, respectively [24]. As all involved species in the formation of the proton hydrates are present continuously in the CLOUD chamber, their peaks are also omnipresent in a typical CLOUD experiment spectrum.

Other peaks which are identifiable in the study are of the kind $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$. This identification is mainly based on Schobesberger et al. [58]. In addition to the standard peaks of this nature, isotopic peaks are found. The most abundant isotope of H_2SO_4 is with an exchanged sulfur atom. One ^{32}S is replaced by one ^{34}S atom. The respective abundance of both sulfuric acid isotopes are 93,9% (^{32}S) and 5,2% (^{34}S). This abundance is high enough for the cluster ions containing the ^{34}S isotope to show up as identifiable peaks in the positive spectrum. As the peak of the isotope cluster ions is higher than what would be expected from only the sulfur isotope, it is assumed that the corresponding peaks are also built up by other, less abundant isotopic sulfuric acid isotopes, containing ^{18}O . Other cluster ions with the same nominal mass as the ^{34}S sulfuric acid molecule but not of $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ nature can also be a reason for a higher than expected intensity of the corresponding peaks. The relative intensity of the isotopic cluster increases with rising n and m in comparison to the standard cluster. This is due to the higher probability of an isotope being present the more molecules the cluster holds. Clusters with more than one isotope of ^{34}S were not found.

Lastly, clusters containing only water and sulfuric acid are found. For these, the ionic species in the cluster is NH^+ . The $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n\text{NH}^+$ cluster are present with n ranging

from 1-3. Here, no isotopic peaks are found.

Other cluster ions cannot be identified. One peak which is visible regularly corresponds to the standard isotope mass of the $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+ + 1$ amu. This peak most likely builds up as a sum of several, similarly abundant isotopes, including the ^{33}S , ^{15}N , and ^{17}O isotopes.

4.2. Mass-Defect Plots

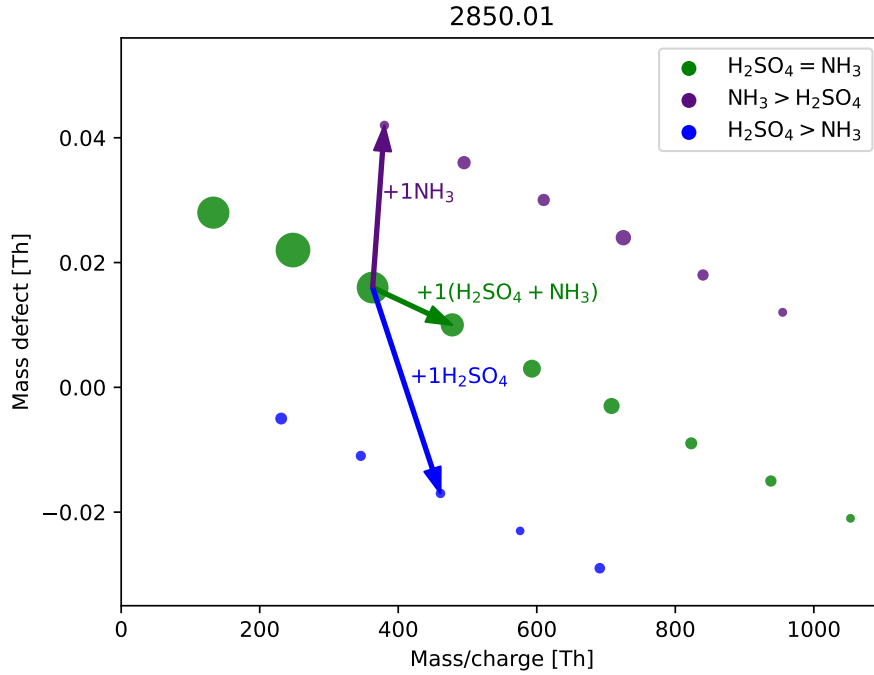


Figure 4.1.: Schematics of an example mass defect plot of the stage 2850.01. The vectors indicate the change a cluster ion peak experiences in its mass and mass defect when another species is added to one cluster. Only $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ peaks are displayed for better visibility.

A standard protocol when analyzing APi-ToF data is to evaluate the mass defect plot. A mass defect plot gives the mass to charge ratio of a cluster on the x-axis (in Thomson units, which equals amu/e) and the mass defect on the y-axis (also in Thomson units). The mass defect describes the difference between a clusters nominal mass and its exact mass. One peak of an average spectrum recorded by the instrument corresponds to one point in the mass defect plot. The size of one point relates to the intensity of the

4. Data Evaluation

recorded peak. As stated in section 2.2, the kinetics of cluster formation suggest that a cluster forms by the successive addition of individual molecules to a nucleation seed. As each of the potentially added molecules has a distinctive exact mass and mass defect, the point of the cluster to which it might be added will shift by the respective exact mass and mass defect in a mass defect plot. This shift in a mass defect plot can be visualized as a vector, as seen in figure 4.1. [58]

The purple vector displays the shift of a parent cluster by the addition of one ammonia molecule, the blue vector the shift by the addition of one sulfuric acid molecule. The green vector displays the shift when both are added to one parent cluster. This method makes for clean overview about how the clusters grow in size in respect to their composition. In this mode of display, more pronounced assumptions can be made about the chemical composition of a cluster ion, by the analysis of the vectors in between different points.

Having discussed how the collected data is processed and analyzed, the results of the experiments can now be presented in the following section.

5. Results and Discussion

The data collected with the positive APi-ToF is analyzed in light of three research questions. The effect of glyoxal on the positive cluster ion spectrum is discussed first, followed by an evaluation of the effect temperature has on the positive cluster ions. Lastly, the difference of spectra recorded under π^+ beam in comparison to ambient GCR conditions is investigated. As stated in section 3.1.1, background measurements of the chamber were conducted. These measurements are evaluated before going into the three research questions, to be able to discuss the effect the chamber background has on the recorded spectra.

For a better overview of the succeeding data, the scheme of names of the experiments shall be explained. The experiments which are held at the CLOUD chamber are each given a "run number". These are upward counting numbers, which have started many years ago, leading to relatively high numbers for the experiments which are discussed in this thesis. A new run (i.e. a new number) indicates a new experiment starting. Each run number also has a stage number, noted after a decimal point. A stage indicates that significant changes have been made to the chamber during an experiment. For example, a data frame titled "2850.01" marks the first stage of the experiment 2850. This universal naming scheme for the CLOUD data makes discussing, comparing and storing of data clear and structured.

5.1. Background Measurements

To have insights on how clean the CLOUD chamber is for the experiments, background measurements were carried out. For this, a spectrum of only sulfuric acid in combination with the synthetic air, water and ozone was recorded. The chamber temperature was set to -30°C , the fans to 12%, relative humidity was at 60%, and two light sabres were turned on.

5. Results and Discussion

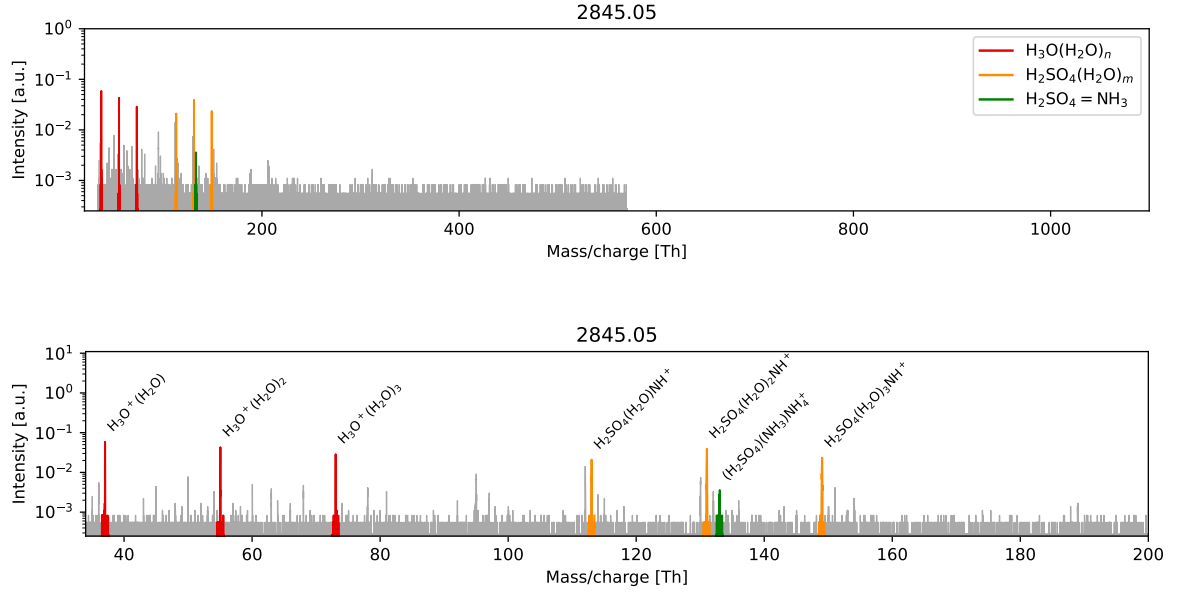


Figure 5.1.: Average spectra of chamber background measurement, stage 2845.05. Top panel displays full mass-to-charge range, bottom panel zooms in on the mass-to-charge range from 35 to 250 Th, with all identified species labeled.

Looking at the background measurement average spectra in figure 5.1, sulfuric acid and water clusters can be observed alongside proton hydrate peaks. These are expected to appear due to the composition of gases present in the chamber. All compounds involved in the formation of the two species are added intentionally during this stage. Furthermore, a few unidentified peaks at low mass to charge ratios with low intensities appear. Because of the unidentified character of them, no statement can be made whether or not they are contaminant species or not. But due to their low abundance, the chamber can be considered sufficiently clean. In addition, there were no above background peaks recorded for mass-to-charge ratios > 200 Th.

Furthermore, the background measurement revealed that even though no NH_3 was being injected, there were still trace amounts of it present in the chamber. This can be seen in figure 5.1, where the green peak displays a sulfuric acid cluster ion also carrying an ammonia molecule (with a 1:1 ratio between H_2SO_4 and NH_3 in the cluster). As other experiments were run in the chamber for several weeks before this study, it is plausible that ammonia from the previous experiments was still on the walls. The spectrum in figure 5.1 was recorded after a full cleaning cycle which involved heating the chamber up to 100°C . Consequently, an ammonia contamination could not be eliminated completely and has to be taken into account when analyzing the following spectra.

5.2. Addition of Glyoxal to a $\text{H}_2\text{SO}_4 + \text{NH}_3$ System

The experimental run 2850 explored the effect of adding glyoxal to an otherwise constant $\text{H}_2\text{SO}_4 + \text{NH}_3$ system in four consecutive concentration steps. The chamber was set to -30°C and had a relative humidity of 60%. The contents in the chamber were continuously mixed on a 12% fan setting and two light sabers emitting at 251 nm were turned on at all times to allow for photochemistry. The sulfuric acid was held constant at $2.3 \cdot 10^6 \text{ 1/cm}^3$ for the first 3 stages, but dropped to $2 \cdot 10^6 \text{ 1/cm}^3$ for the last stage. The ammonia content in the chamber during the experiments ranged from 680 pptv to 770 pptv. Glyoxal was added to the chamber for the last three of the four stages in the following respective concentrations: 27 pptv, 124 pptv, and 487 pptv. The first stage was held without intentional addition of glyoxal, the background level was at 6 pptv. Note that the units pptv and 1/cm^3 both indicate concentration values of molecules and can easily be converted to one another ($1 \text{ pptv} = 2.46 \cdot 10^7$) [59]. To stay comparable, for each species, the unit which is used in literature will also be used in this thesis. Each stage was conducted for 2-3h. Moreover, the signal-to-noise ratio varies with each stage as this depends mainly on the time a stage was measured for.

5.2.1. Run 2850, Stage 1: Pure $\text{H}_2\text{SO}_4 + \text{NH}_3$ System

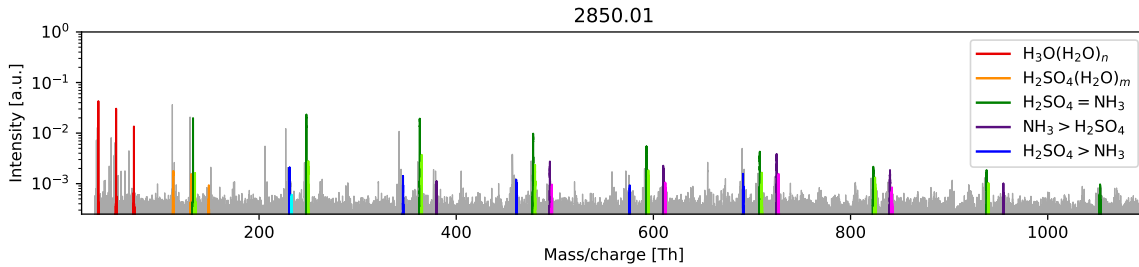


Figure 5.2.: Average spectra of stage 2850.01.

Stage 2850.01 was held as a comparison to when glyoxal is added to the chamber, hence the glyoxal concentration was at background level. The average spectra (figure 5.2) as well as the mass defect plot (figure 5.3) show a distinctive cluster pattern. The red points (and peaks) depict the proton hydrate clusters, and the orange points the sulfuric acid + water clusters. All other colored points are of the type $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$, i.e. clusters containing sulfuric acid and ammonia molecules with an ammonium ion carrying the positive charge. It can be postulated that the charge carrying ion is H^+

instead of NH_4^+ , and the number of ammonia molecules are increased by one for each cluster, as this would lead to the same nominal mass. This however is contrary to literature ([58, 60]), where NH_4^+ is found as the charge carrying ion for sulfuric acid and ammonia clusters. NH_4^+ is expected to act as a weak acid in the clusters. More positive cluster ions have been recorded, but could not be identified in their respective chemical composition (gray points).

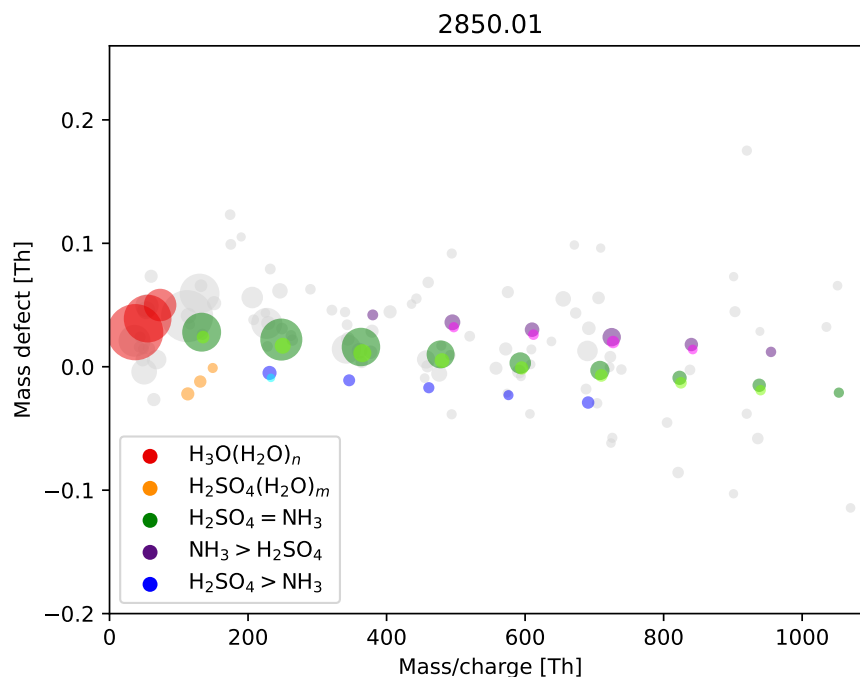


Figure 5.3.: Mass defect plot of the pure sulfuric acid and ammonia system (2850.01), before addition of glyoxal.

Colored in dark green are the points corresponding to clusters of the type $n = m$. These show up as local maxima in intensity over a broad range in the mass spectrum. The values of n (and m) for detected cluster are $1 \leq n \leq 9$. The light green points are of the same character, but carry the ^{34}S isotope of sulfur.

The purple points depict the ion clusters which have an $m = n + 1$ characteristic composition. Hence, they carry more ammonia than sulfuric acid molecules. They only start to appear for $n \geq 3$ clusters but can be detected for up to $n = 8$. Also here, the pink points depict clusters with one sulfur isotope.

The blue points correspond to clusters which are composed of more sulfuric acid molecules than ammonia, therefore $n = m + 1$. The smallest cluster which appears of

this kind is a $n = 2$ cluster, i.e. it holds two H_2SO_4 molecules and one NH_3 molecule. The biggest cluster ion detected of this character is for $n = 6$. Again, the light blue point is a cluster of the same $n = m + 1$ characteristic, carrying one ^{34}S atom.

It can be observed that the cluster ions of the type $n = m$ appear over the broadest mass range and at highest intensities except for water clusters. Positive cluster ions which carry more sulfuric acid than ammonia start to appear from their smallest possible size of $n = 2$ but are not detected towards the higher end of the mass range. For the ammonia dominant cluster ions, the behavior is the opposite. Here, the cluster ions are not detectable in their smallest possible composition of $n = 1$, nor for the $n = 2$ case, but they stay detectable for the higher mass ranges. They reach a comparable upper mass limit as the $n = m$ case.

Another finding is that only clusters with a maximum difference in ammonia and sulfuric acid concentration of one molecule were observed.

This cluster pattern is a prime example of the base-stabilization nucleation mechanism described in Kirkby et al. [5] and section 2.2.4. The study shines light on how a step-wise accretion of NH_3 molecules to an otherwise H_2SO_4 containing cluster stabilizes the formation pathway of particles. The paper mostly focuses on the negative cluster ions showing this formation pattern. With the APi-ToF measurements conducted during the CLOUD17 campaign, the pattern is observed for the positive ion nucleation pathway. In the spectrum of experiment 2850, binary clustering of sulfuric acid and water has also been recorded (orange points). But their growth is very limited, with only clusters of one sulfuric acid molecule with up to three water molecules being observed. The strong appearance of the $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ type clusters in comparison to the absence of bigger pure binary sulfuric acid and water clusters therefore underline the statement made in Kirkby et al. [5], that the growth involving ammonium bisulfate ($\text{NH}_4^+\text{HSO}_4^-$) is the most stable.

5.2.2. Run 2850, Stages 2-4: Evolution of the Cluster Ions under Addition of Glyoxal

When looking at the stages where glyoxal is being added to the $\text{H}_2\text{SO}_4 + \text{NH}_3$ system, a general decrease in the number of peaks and their intensity can be observed. This trend can be seen especially well for the example of the $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ clusters. They decrease in abundance when glyoxal concentrations are increasing, indicating a suppres-

5. Results and Discussion

sion of formation of such clusters by the addition of glyoxal. Figure 5.4 visualizes this behavior by displaying the intensity of the $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ clusters over glyoxal concentration for each stage held.

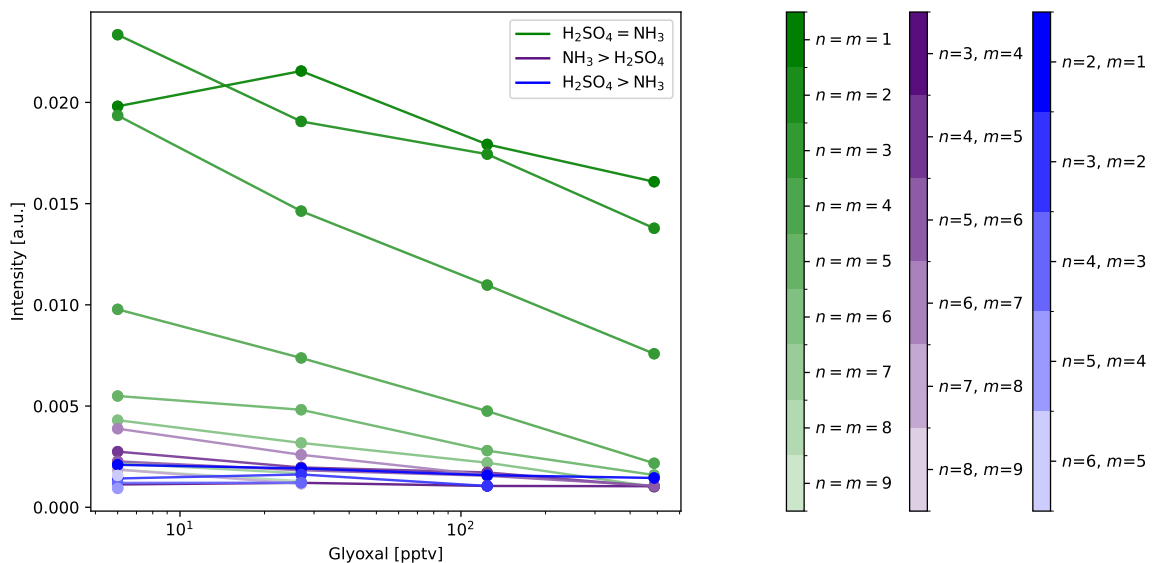


Figure 5.4.: $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ cluster peak intensity vs. glyoxal concentration from the experiment 2850 (ramping of glyoxal). The glyoxal concentrations during the experimental stages were; 01: 6 pptv, 02: 27 pptv, 03: 124 pptv, 04: 487 pptv. n gives the number of H_2SO_4 molecules per cluster, m the number of NH_3 molecules.

One other key finding is that no new positive cluster ion species form with the injection of glyoxal to the chamber. This is pictured in figure 5.5, which displays the difference in peak intensity Δ of the two average spectra of 2850.01 and 2850.04. A positive Δ relates to a dominance in abundance of a species in the first stage. It is clearly visible, that the stage 4 has little to no species which are more abundant than in the stage 1. The significant dominance of ammonia and sulfuric acid carrying clusters in the first stage is also underlined in this plot. It can be concluded that the addition of glyoxal suppresses the formation of positively charged sulfuric acid and ammonia cluster ions, while also not forming positive cluster ions that are composed of the organic species.

Despite the decrease of positive cluster ions under the addition of glyoxal, an increase in J-rate can be observed. From 6 to 487 pptv of glyoxal, the $J_{1.7}$ doubles. $J_{1.7}$ refers to the nucleation rate for particles bigger than 1.7 nm being produced. This indicates that other nucleation paths (neutral and/or negatively charged) rise in importance and must contain increased cluster abundance under the addition of glyoxal to a $\text{H}_2\text{SO}_4 + \text{NH}_3$

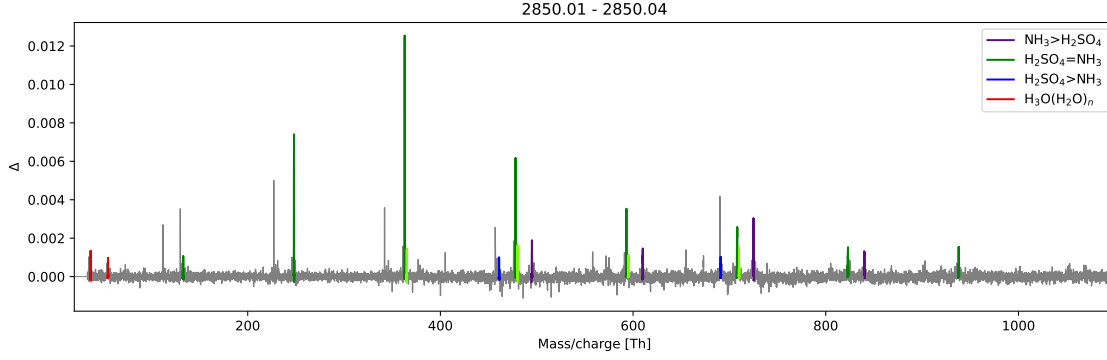


Figure 5.5.: Difference between the two average spectra of 2850.01 and 2850.04. A positive value of a peak indicates that the species has a higher concentration in the 2850.01 stage, a negative value indicates the opposite.

system.

5.2.3. Discussion of Glyoxal Experiments

$(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ Peak System

As presented above, the $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ clusters can be observed nicely during the experiment 2850. A prominent finding is that the charge carrying ion is always NH_4^+ . For positive ion clusters in general, another important ion is H^+ [24]. H^+ however is not found in combination with the ammonium bisulfate formation pathway. Moreover, as described in section 5.2.1, a shift in appearance (in reference to the mass/charge axis) between the ammonia dominant vs the sulfuric acid dominant clusters can be seen. The sulfuric acid dominant clusters appear for smaller masses and cannot be detected towards the higher end of the mass axis, while the ammonia dominant ones are present for higher masses, but not at the smaller end of the mass axis. The same behavior was also observed in Schobesberger et al. [58]. It can be concluded, that even though the most stable new particle formation pathway stays at the molecular ratio of 1:1 between H_2SO_4 and NH_3 , a bigger cluster can tolerate an excess of ammonia more efficiently, while a smaller cluster tolerates more sulfuric acid.

Kirkby et al. [5] discussed the negatively charged $\text{H}_2\text{SO}_4+\text{NH}_3$ nucleation in their study, in which experiments with ammonia concentrations of up to 230 pptv were carried out. Ammonia concentrations during the study discussed in this thesis were around three times higher. A comment made in the Kirkby et al. [5] paper reveals that they have

also observed positive nucleation of said formation pathway, at higher ammonia concentrations than of the system investigated for the negatively charged pathway. Thus, the measurements conducted during CLOUD17 are coherent with the finding of Kirkby et al. [5]. A difference compared to the findings of Kirkby et al. [5] is that in the CLOUD17 study, the concentration of $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ peaks decreases for an increasing number of molecules on the cluster ion. It is to be noted, that the two studies used different APi-ToF models. [5] utilized an Aerodyne instrument while the instrument used for this thesis is from Ionicon. As the two instruments differ in resolution and transmission, differences in the recorded spectra can appear, even at identical conditions. The comparatively low transmission efficiency of the Ionicon instrument also decreases for increasing mass to charge ratios, which could explain the observed difference described above.

Application to the ATAL

The motivation of the experiment was to explore the formation of new particles in the Asian Tropopause Aerosol Layer (ATAL). Ergo, it is important to discuss how applicable the measurements carried out in the chamber are to the atmospheric system of interest. The ATAL is an air mass containing enhanced number of particles and was first observed in the late 2000s. CLOUD17's glyoxal experiments aimed to investigate whether or not glyoxal plays a significant role in new particle formation in the ATAL, thus contributing to the observed high particle concentrations. Johansson et al. [61] presents data of aircraft measurements which recorded the abundance of trace gases in the ATAL. They revealed enhanced ammonia concentrations of up to 1.5 ppbv, with an average of around 800 pptv. Hence, the ammonia concentrations present during the chamber experiment (~ 730 pptv) are representative of the ATAL. The interpretation of the sulfuric acid concentration is more difficult, as no in-situ measurement of H_2SO_4 has been made. Sulfuric acid concentrations in similar altitudes over Europe have been measured by Zauner-Wieczorek et al. [62] to around $1 \cdot 10^6$ $1/\text{cm}^3$. Ma et al. [44] predicts no enhanced sulfuric acid concentrations for the ATAL due to the convective uplifting. Based on this, the European tropopause concentrations of sulfuric acid can be viewed as an indication for said levels in the ATAL. Thus, concentrations during the chamber experiment are slightly enhanced ($\sim 2.2 \cdot 10^6$), but still in the same order of magnitude, resulting in comparable conditions. It therefore follows that the results from CLOUD17 can be applied to make statements about the processes in ATAL.

In conclusion, the experiment exploring a glyoxal, ammonia and sulfuric acid system

showed, that the new particle formation induced through positive ions does not explain the enhanced particle concentrations in the ATAL. However, an increase in J-rate can be observed when glyoxal is added to the system, indicating that either the negative ion induced new particle formation or the neutral production pathway enable the observed increased concentrations.

5.3. Temperature Dependence

To analyze the temperature dependence of the positive cluster ion spectrum, experiment 2850.01 and 2855.14 were chosen to be compared, as these were held at comparable conditions with the only difference being the chamber temperature. The temperature during the stages 2850.01 and 2855.14 was set to -30°C and -50°C , respectively. The trace gases present during these runs were only sulfuric acid and ammonia, but no glyoxal. Further information about the conditions within the chamber can be found in the appendix in table A.1.

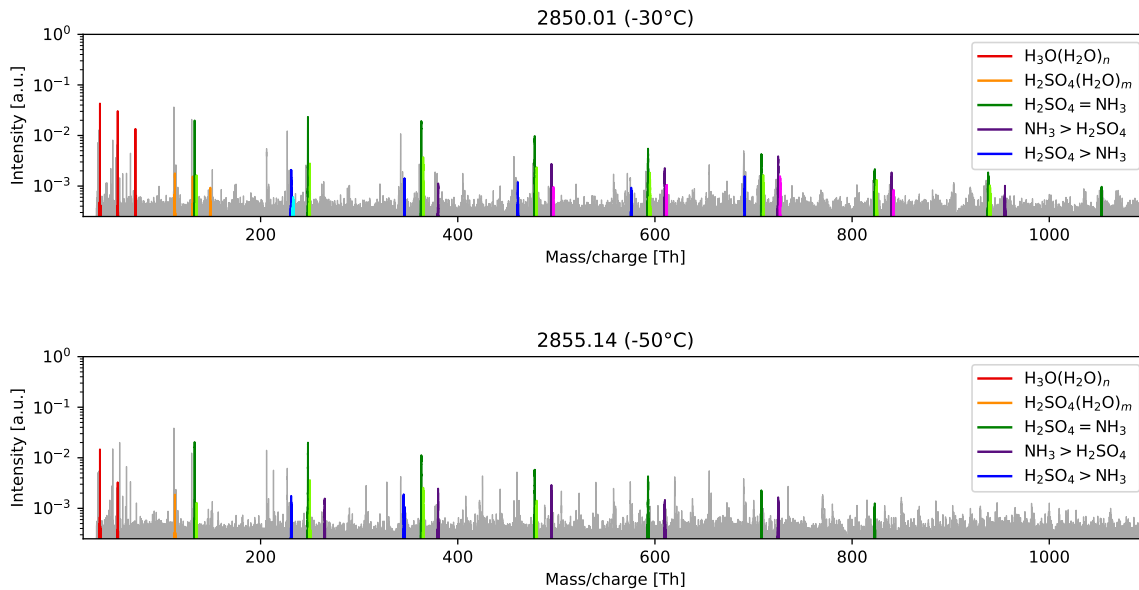


Figure 5.6.: Average positive cluster ion spectrum of stage 2850.01 (-30°C) and 2855.14 (-50°C). The gray peaks are unidentified and show a new peak pattern arising in the -50°C spectrum.

One finding is the disappearance of the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ $n = 3$ peak when the temperature is being reduced to -50°C . As elaborated in section 4.1, these are the dominant

positive cluster ions in the lower atmosphere. The proton hydrates are found in the atmosphere with one to three water clusters [24]. During the entirety of measurements at CLOUD17, the APi-ToF had a clear signal of the proton hydrates with $n = 1, 2, 3$. The measurements at -50°C show the only clear deviation of the proton hydrate signal. Not only does the $n = 3$ cluster disappear, but the $n = 1, 2$ clusters also have a significant decrease in intensity, compared to the spectrum measured at -30°C .

$(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ peaks appear at both temperatures, though the abundance of them is more pronounced in the warmer system. Especially the bigger clusters decrease in intensity.

Lastly, a new peak pattern can be observed at -50°C . The average spectra seen in figure 5.6 depicts new peaks arising from around 300 Th and bigger. The periodicity between the peaks is alternating between 17 and 18 Th. Analyzing the mass defect plot of the experiment 2855.14 reveals that, most likely, one ammonia and one sulfuric acid molecule condense onto the pre-existing parent clusters. This is another demonstration of the acid-base-stabilization mechanism [5]. The addition of the two molecules onto a parent cluster can be retraced when looking at the vectors that lie in between two points of the mass defect plot, as seen in figure 5.7. They have about the same magnitude as that between a $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ and a $(\text{H}_2\text{SO}_4)_{n+1}(\text{NH}_3)_{m+1}\text{NH}_4^+$ peak. Also the orientation of the vectors is nearly identical, though a slight deviation is visible here. This deviation lies within the resolution of the instrument and is expected to disappear if the clusters are identified. In this case, their exact mass would be applied in the peak list, resulting in a slight shift of the points in the plot. Still, the new peaks could not be identified, since the mass of the clusters deviate from the pure $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ clusters. The embryo on which the NH_3 and H_2SO_4 molecules condense onto is what remains unknown.

5.3.1. Discussion of Temperature Experiments

When comparing the decreasing intensity of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ peaks during the experiment with literature, there seems to be a discrepancy. The third order rate coefficient of the reaction forming $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ has a negative dependence on T, indicating that the reaction rate increases with decreasing temperature [63]. This should lead to enhanced concentrations of the proton hydrate peaks. On the other hand, classical nucleation theory dictates that nucleation rates increase with decreasing

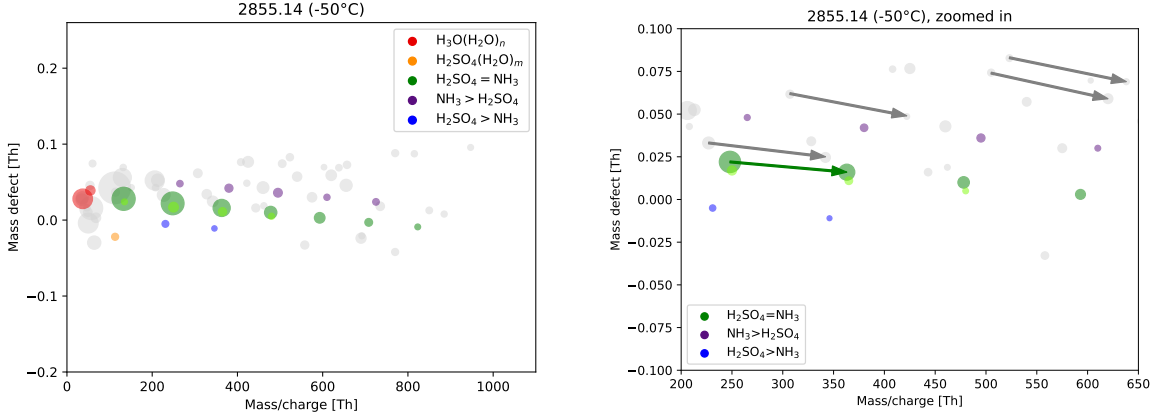


Figure 5.7.: Mass defect plot of stage 2855.14. The proposed addition of one sulfuric acid molecule and one ammonia molecule to otherwise unknown cluster peaks is indicated by gray vectors, the green vector displays the known shift of a peak by the addition of said molecules.

temperature. This comes to be as the saturation ratio S of a system increases with decreasing temperature, because of a decreasing equilibrium vapor pressure p_{sat} [28]. This was demonstrated by different studies, which investigated the temperature dependence of new particle formation events [5, 6, 64]. The negative cluster ion spectrum does not indicate a similar change in behavior.

As mentioned above, the system at -50°C shows a new peak pattern, with overall more peaks than the -30°C system has. It can be argued that the lack of concentration of the known $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ peaks has been shifted to the new peak pattern. Furthermore, the J-rate between the two stages 2850.01 and 2855.14 are equal, meaning that the same number of particles are produced per second per cubic centimeter in both systems. The total ion count in the positive API-ToF is lower for the colder system than for the warmer. This suggests that the positive ion nucleation pathway is not enhanced for this system. Therefore, either the negative or the neutral new particle formation pathway should show increased cluster levels.

The temperature of the ATAL is closer to that of run 2855 (-50°C). Hence, the newly arising peaks for that temperature are of significant interest for the overall understanding of new particle formation in the region.

5.4. Effect of the Proton Beam

To recreate atmospheric conditions of higher ion densities as they are found in the upper troposphere/lower stratosphere, CERNs π^+ beam from the Proton Synchrotron can be utilized. It can create ion pair concentrations of around 3000 1/cm^3 within the chamber. For this section, two different experiments are analyzed in respect to the effect the π^+ beam has on the positive cluster ion spectrum. During the experiment 2855, the stages 20 and 21 were held under GCR ($\sim 400 \text{ ion pairs per cm}^3$) and beam conditions, respectively. For both stages, sulfuric acid, ammonia and glyoxal were injected to the chamber at equal levels. The chamber temperature was set to -50°C and RH was at 100%. More details of the chamber conditions can be found in table A.1. The second experiment which is investigated is experiment 2846. Here, the stages 4 and 5 were held under GCR and beam conditions, respectively. Experiment 2846 had a chamber temperature of -30°C and an RH of 60%. Sulfuric acid and glyoxal were injected into the chamber with constant concentrations, but no ammonia.

5.4.1. Run 2855.20 vs. Run 2855.21

The GCR stage of run 2855 shows a spectrum with only a few peaks above background. The highest intensity measured is for an unidentified peak at around $2.6 \cdot 10^{-2}$ a.u. (arbitrary units). Only the $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ peak could be identified, alongside the $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ peaks with $n = m = 1, 2, 3, 4$. The beam stage of this experiment shows a more detailed spectrum, with more peaks appearing above background levels. The highest intensity measured during this stage is around $2.2 \cdot 10^{-1}$ a.u. and at the same mass to charge ratio as the highest intensity peak of the GCR stage. Both average spectra can be seen in figure 5.8. It should be noted that the two stages were held for comparable measurement times.

5.4.2. Run 2846.04 vs. Run 2846.05

The comparison between the GCR and beam stages of experiment 2846 show a different behavior than that of the 2855 experiment. This can be seen best in their respective mass defect plots. Note that the mass defect plots of stage 2846 have an adjusted scaling factor that relates peak intensity to point size, which differs from the other mass defect plots seen in this thesis. The scaling factor is decreased by one magnitude to allow for

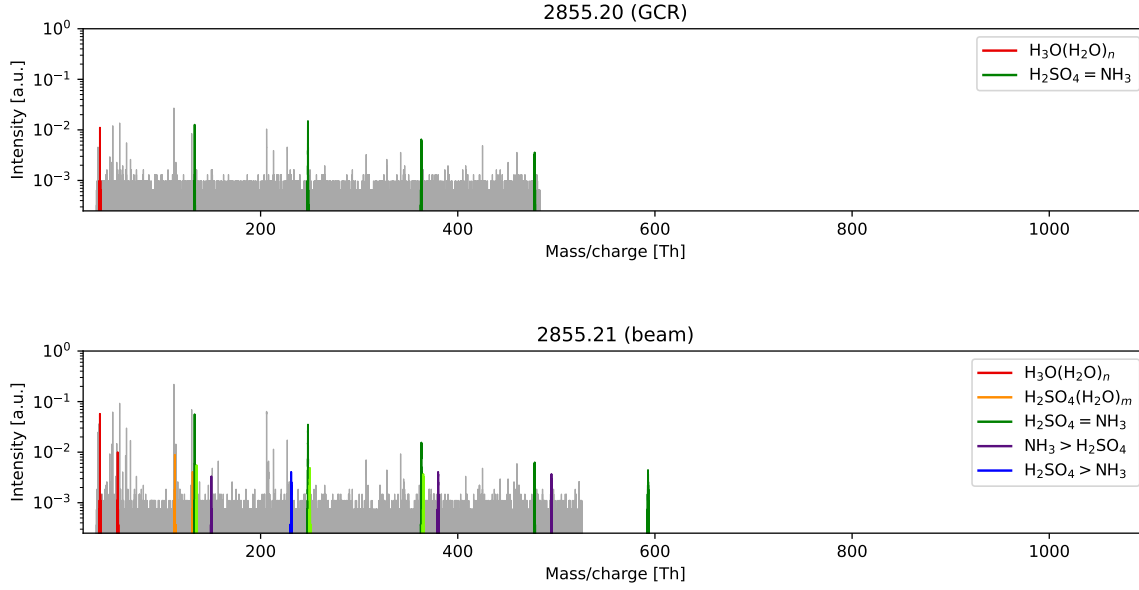


Figure 5.8.: Average ion cluster spectrum of stage 2855.20 (GCR, top panel) and 2855.21 (beam, panel).

a more detailed spectrum to be seen, as the intensities of individual peaks during the beam stage are so high that they would otherwise overlap with and hide other peaks.

A comparison between the mass defect plots (see figure 5.9) of the two stages shows a group of unidentified peaks appearing around 400 Th for the GCR stage. This group of peaks is decimated for the beam stage spectrum. A few peaks with slightly enhanced concentrations remain, but most of them disappear. On the other hand, for smaller peaks up to around 200 Th, the number of peaks which are detected during the beam stage is increased, in comparison to the GCR stage. None of the newly appearing peaks in the beam stage could be identified. Hence, no statement about their chemical composition can be made.

Clearly noticeable are also the increased intensities of the $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_m\text{NH}^+$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ peaks. The spectra of the two stages exhibit that under GCR conditions, a $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_m\text{NH}^+$ peak with $m = 4$ water clusters can be found. In comparison, during the beam stage the biggest $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_m\text{NH}^+$ cluster measured had $m = 3$ water molecules.

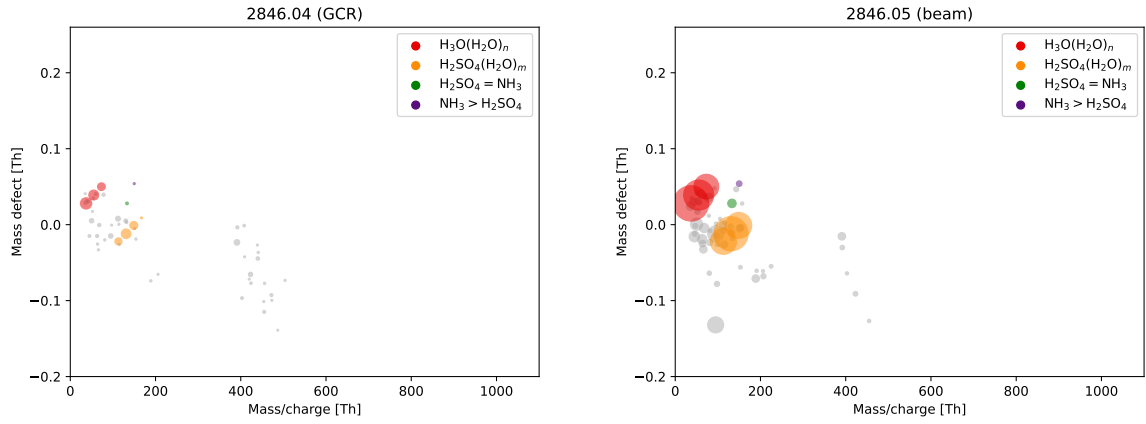


Figure 5.9.: Mass defect plots of the two stages 2846.04 (GCR conditions) and 2846.05 (beam conditions).

5.4.3. Discussion of Proton Beam Experiments

The difference in spectra between the stages 2855.20 and 2855.21 is clear in the sense that the enhanced ion pair concentration leads to an increase in intensity of the cluster ions in the chamber. Even though the spectrum of the stage 2855.20 (GCR) only has a few peaks above background, it seems that the enhanced ion pair concentration in the beam stage leads to a more pronounced spectrum of the same structure as that of the GCR stage. As a similar composition of trace gases were also present during the stages 2850.02 and 2850.03, one can compare the 2855.21 spectrum to those as well. This comparison leads to the same conclusion, that the beam stage 2855.21 shows the same structured spectrum as that of the GCR stage, only with more peaks being above background occurring due to higher ion pair concentrations. No peaks of new compositions as known for that system seem to be evolving, neither do the bigger peaks disappear.

For the experiment 2846, this cannot be stated. As mentioned in the previous section, some of the positive cluster ions around 400 Th detected during the GCR stage cannot be found in the subsequent beam stage, even though both stages had equal chamber conditions. This is contradictory to the expectation that from the enhanced ion pair concentration, the spectrum reveals enhanced intensities of already present clusters. Alongside peaks of bigger mass to charge ratios disappearing, new peaks appear for smaller Th. With this observation, the question of doubly charged cluster ions arises. A cluster of double the charge for the same mass would lead to exactly half the mass to

charge ratio. None of the disappeared peaks show up at half their mass to charge ratio, disproving this hypothesis. Also, the ions self repulsion prevents doubly charged cluster ions for the most part [27]. For this system of trace gases, no other reference spectra has been recorded. Hence, no further comparison of the 2846.05 spectrum can be made.

This observation of changed spectra under beam conditions indicates a not yet known difficulty. One explanation for the disappearance of the bigger peaks could be, that the doubly charged clusters do form, but are not stable and quickly tear up into two clusters because of the ions self repulsion. The resulting two smaller cluster ions do not need to be of equal mass. This could then in turn explain the newly appearing, unidentified peaks at around 200 Th. Why this is not observed for the stage 2855 can not be explained.

For both experiments (2846 and 2855), the J-rates during the beam stage was increased compared to the GCR stage. During experiment 2855, the J-rate increased by around a factor of 1/3, while the increase during the 2846 experiment was around a factor 2.

The processes under beam conditions are especially interesting for the ATAL, as the layer is located in altitudes where the ion pair concentrations are similar [48]. This underlines a special interest for further research of the unexplainable processes observed.

5.5. Experimental Difficulties

Despite CLOUD being a state of the art experiment, some difficulties remain when it comes to chamber based investigation of new particle formation. One of them revolves around the concentrations of trace gases in the chamber, and how they can be held constant whilst partaking in chemical reactions continuously. As sulfuric acid is not added directly to the chamber like described in section 3.1.1, holding it stable relies on several components simultaneously. This resulted in the slightly variable concentrations of H_2SO_4 during the experiment 2850. Between the third and the fourth stage, the concentration dropped from $2.3 \cdot 10^6$ to $2 \cdot 10^6$ $1/\text{cm}^3$. But as the fluctuation is minor compared to the absolute concentration, it can be neglected. This argument is underlined by literature, as such fluctuations lie in the variability of given sulfuric acid concentrations for atmospheric systems. [5, 65]

The same problem can be discussed for ammonia and glyoxal. Even though both are added to the chamber directly, they are still prone to fluctuations, as they can partake in chemical reactions within the chamber, influencing their concentration. The variation of ammonia content is higher compared to that of sulfuric acid in relative terms, but again, the values lie in a range which represents the same atmospheric conditions. [61, 66, 67]

A further difficulty is the general chamber background. As elaborated in section 5.1, the chamber had some ammonia contamination before the start of the experiments. It was reduced as far as possible, but a minor contamination remained.

5.6. Performance of the APi-ToF

Alongside experimental difficulties arising due to the chamber, the measurement instrument itself can also majorly influence the reliability of the data.

For the APi-ToF, the transmission efficiency η was the main difficulty. As mentioned in section 3.3.1, the instrument was tuned on site at CERN during the CLOUD17 campaign. Thus, optimal performance of the instrument for the local conditions was realized. This tuning was not altered for the subsequent transmission efficiency measurements in the lab in Vienna. The measurements carried out in the lab determining η resulted in smaller values than what is found for comparable instruments in literature. As external

factors like temperature and passing time in general influence the instruments transmission efficiency, it is very likely that η has declined between the measurement campaign at CERN and the transmission efficiency measurements at the lab. Therefore, better transmission efficiencies can be assumed for the CLOUD17 measurements. Moreover, the spectra recorded with the APi-ToF of the University of Vienna delivered highly detailed spectra, which were similarly if not more detailed than comparable spectra of other instruments during the campaign. This indicates a sufficient transmission efficiency.

The instruments mass calibration also seemed to be sufficient, as known peaks always matched up with their respective mass to charge ratio. The discrepancy between expected m/z and measured m/z was in a range of ± 0.2 Th. This could be corrected for during the post processing of the data.

6. Conclusion

This thesis discussed the data collected with the positive APi-ToF during the glyoxal experiments of the CERN CLOUD experiment in the fall of 2024. The three research questions raised in the introduction have been discussed in light of three different experimental runs.

The first question, of how the positive cluster ion spectrum changes when glyoxal is added to an ammonia-sulfuric acid system, was answered by the experiment 2850. It was revealed that an addition of glyoxal to a constant ammonia and sulfuric acid system suppresses the formation of $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m\text{NH}_4^+$ cluster ions. Moreover, the base-stabilization nucleation mechanism was observed in the positively charged pathway.

The second question investigated the effect temperature has on the positive cluster ion spectrum. The experiments demonstrated that new positive cluster ions are forming when the temperature is reduced from -30°C to -50°C , while others are disappearing. This data depicts a change in nucleation pathway for a change in temperature, which could also hint at a change in chemical reactions occurring.

The last question analyzed the effect of the CERN Proton Synchrotron π^+ beam on the positive cluster ion spectrum. Two different experiments showed two different effects of the beam. One (run 2855) behaved as expected with the enhanced ion pair concentration, and showed increased cluster ion signals for the same cluster compositions. The other (run 2846) displayed an unexpected discrepancy between the spectra of GCR and beam conditions. Some peaks of clear signal at the GCR stage were no longer found for beam stage, while other new peaks were also appearing during the exposure of the beam. A break up of the bigger positive cluster ions can be proposed as an explanation of this observation.

A conclusion which can be drawn for the question of how new particle formation in the ATAL occurs, is that the positive ion nucleation pathway seems to play an insignificant role. This is underlined by experiment 2850, where the positive cluster ions are being

6. Conclusion

suppressed by the addition of glyoxal. Moreover, no cluster ions composed of glyoxal or related species can be detected.

Further research is needed to make reliable predictions on how the particles form in the ATAL. For this, additional variations of the same system (different concentration of trace gases for different temperatures) need to be explored to represent a full picture and parameterization of the aerosol layer. With this knowledge, the impact of emissions on aerosols, clouds and hence the climate can be assessed, modeled and regulated in order to improve our options to mitigate climate change.

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Appendices

A. Tables

Run number	Temperature [°C]	RH [%]	GCR/beam	NH ₃ [pptv]	H ₂ SO ₄ [1/cm ³]	Glyoxal [pptv]
2845.05	-30	60	GCR	<30	$4.7 \cdot 10^6$	<1
2846.04	-30	60	GCR	<30	$4.2 \cdot 10^6$	567
2846.05	-30	60	beam	<30	$4.2 \cdot 10^6$	580
2850.01	-30	60	GCR	680	$2.3 \cdot 10^6$	6
2850.02	-30	60	GCR	710	$2.3 \cdot 10^6$	27
2850.03	-30	60	GCR	770	$2.3 \cdot 10^6$	124
2850.04	-30	60	GCR	715	$2.0 \cdot 10^6$	487
2855.14	-50	100	GCR	710	$2.8 \cdot 10^6$	2
2855.20	-50	100	GCR	780	$2.9 \cdot 10^6$	71
2855.21	-50	100	beam	680	$2.3 \cdot 10^6$	70

Table A.1.: Settings and concentrations of gases in the CLOUD chamber during the experiments of interest.

B. Figures

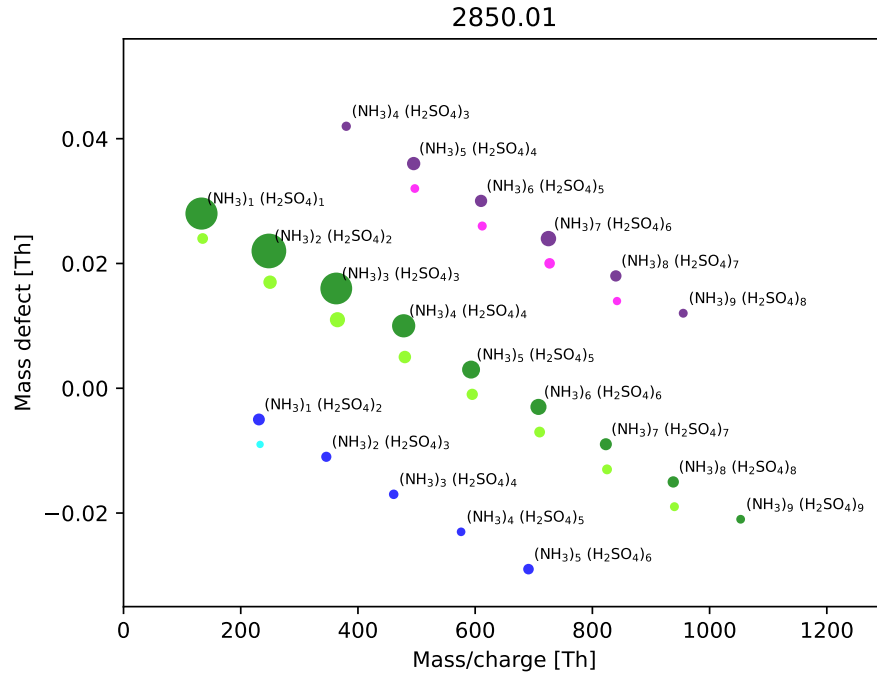


Figure B.1.: Example mass defect plot of the stage 2850.01 with labeled species. The data points in pink, light green and light blue indicate the same molecular composition of a peak like the neighboring darker peak, but with one ^{32}S atom being replaced by the ^{34}S isotope, leading to a slightly higher mass of the cluster ion.