Influences of ice particles on the ion chemistry of the polar summer mesosphere

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Abstract. In the polar summer mesosphere, charge is distributed over a wide range of constituents closely connected to phenomena like noctilucent clouds and polar mesosphere summer echoes. In this paper we study how the presence of ice particles influences mesospheric ion chemistry, and how this may feed back on the particle population. To this end, we present an ion-chemical model that for the first time features close coupling with cluster growth and ice particle charging. Starting out from molecular ion reactions, the H+(H2O)n proton hydrate chain is described using the Thomson model and Natanson's recombination scheme. Under most mesospheric conditions electron capture by particles is expected to enhance the lifetimes and concentrations of positive ions and clusters. This has important consequences for the total charge density and mobility in the environment of particle layers. Extending the proton hydrate chain to large cluster sizes, we also quantify the efficiency of ionic nucleation of mesospheric ice particles. While ionic nucleation is not feasible as the major mesospheric nucleation process, it can become efficient given moderate atmospheric variations as induced by gravity waves. This leads to a scenario of rapid generation of populations with many small particles in local temperature minima. We show that electron capture to existing particles can significantly enhance the ionic nucleation of new particles. In summary, there are many potential connections between ion chemistry and layered phenomena in the mesosphere that should be included in comprehensive models of NLC/PMSE. Unfortunately, uncertainties in ionic reaction rates are a persistent problem and in great need of laboratory measurements representative for cold summer mesopause conditions.

1. Introduction

The summer mesopause region at high latitudes is a complex ion-chemical environment where light ions, clusters and ice particles interact in various ways. This environment coincides with the ionospheric D-region that features drastic changes in charge density and ion composition over vertical scales of a few kilometers. Comprehensive models of this ion chemistry have been developed e.g. by Reid [1976], Kopp [1996], and Turunen et al. [1996]. These models involve ion-chemical schemes with of the order of 50 positive and negative ions and ion clusters. Below a transition altitude of 80-90 km, a general feature is the conversion of light ions, primarily NO+ and O2+, into oxonium clusters (or "proton hydrates") H+(H2O)n. Reid [1989] discussed D-region ion chemistry with particular focus on the very cold conditions near polar summer mesopause. Here, at temperatures of 130 K and below, heavy proton hydrates (n > 6) can gain importance and give rise to significant changes of the plasma properties [Björn and Arnold, 1981; Sugiyama, 1994].

In the same region of the atmosphere, charging processes are closely connected to a variety of layered phenomena involving icy particles. Most prominent among these are Noctilucent Clouds (NLC) and Polar Mesosphere Summer Echoes (PMSE) [Thomas, 1991; Cho and Röttger 1997]. A long list of rocket-borne and ground-based campaigns have been dedicated to these phenomena. Related in situ observations of layered charge features include electron bite-outs [Ulwick et al., 1988], ion enhancements and bite-outs [Balsiger et al., 1996; Lübken and Rapp, 2001], cluster ions [Goldberg and Witt, 1977; Björn et al., 1981], charged particles of either sign [Havnes et al., 1996], as well as small-scale fluctuations of charge [Lübken et al., 1993] and electric fields [Pfaff et al., 2001].

Interactions between ion chemistry and the existence of icy particles are mutual. Icy particles influence ion composition and reaction scheme by capture of electrons and ions [Natanson, 1960; Parthasarathy, 1976], Charges and charged particles, on the other hand, can influence the particle growth, in particular coagulation processes [Jensen and Thomas, 1991; Reid, 1997] or the particle shape resulting from condensation. Moreover, proton hydrate clusters have been suggested as possible condensation nuclei for ice particles [e.g., Witt, 1969; Arnold, 1980]. A detailed mechanism for nucleation on proton hydrates has been outlined by Sugiyama [1994]. However,
based on current knowledge meteoric smoke particles rather than cluster ions are thought to serve as dominant condensation nuclei in the mesosphere [Turco et al., 1982; Keese, 1989]. The groundbreaking work of Turco et al. [1982] combined both smoke and ionic nucleation in a coupled ice particle model for the mesosphere. This work showed that in the direct competition between both nucleation mechanisms, supersaturation requirements for condensation on smoke particles are significantly less restrictive. Ionic nucleation can only become an efficient competitor at extremely low temperatures; the generation of large numbers of small (sub-visible) particles becomes the most likely scenario under those conditions. Many later NLC models have completely focused on condensation onto the meteoric nuclei [e.g., Jensen and Thomas, 1988; Klostermeyer, 1998]. This choice is also supported by recent simulations of ice particle growth and detailed water budget by Berger and von Zahn [2002] and von Zahn and Berger [2002]. These authors suggest a very efficient freeze-drying of the NLC/PMSE region, with water ice redistribution both vertically and equatorward. This would result in persistent dehydrated conditions near the summer mesopause, thus further limiting the feasibility of ionic nucleation. On the other hand, a caveat of nucleation on meteoric material remains the fact that the existence and properties of meteoric smoke particles as proposed by Hunt et al. [1980] are still in lack of experimental verification in the mesosphere.

With the present work, we study the effect of mesospheric icy particles from an ion-chemical point of view. We investigate how ion reactions and ion composition are changed in the presence of particles. A model that aims to describe these processes must combine basic ion chemistry, clustering processes as well as charge capture by particles. Our OASIS model (Originally Austrian Study of the Ionosphere) is based on an ion-chemical code originally developed by Torkar and Friedrich [1983]. The ion chemistry scheme is similar to the standard models listed above [Reid, 1976; Kopp, 1996; Turunen et al., 1996]. The Thomson droplet description [e.g., Holland and Castleman, 1982] is applied to describe cluster growth to the larger sizes. The interaction of particles and light charge carriers is included based on the formalism by Natanson [1960]. Finally, the ideas developed by Arnold [1980] and Sugiyama [1994] are used to allow for cluster growth towards condensation nuclei for ice particles. This fills the size gap between molecular ions on the one hand and particles of radii exceeding 1 nm on the other.

It is important to note that our model is not an ice particle growth model for NLC or PMSE. A complete, interactive ice particle model for the mesosphere must include transport processes (advection, sedimentation) and time-dependent feedback on the neutral atmosphere, in particular on the water budget [Turco et al., 1982; Jensen and Thomas, 1994; Rapp et al., 2002]. This is beyond the scope of our steady-state ion-chemical model. Ice particle layers are introduced only as input to the simulations; the model is concerned with their effect rather than with their origin. Nevertheless, the OASIS model is able to provide important information about the first step of particle evolution, i.e. particle nucleation. We show that ionic nucleation rates can be enhanced drastically when particle influences on the ion chemistry are present.

Chapter 2 of this paper provides a description of the OASIS model and discusses relationships to earlier models of D-region chemistry, clustering and particle charging. Sections 2.1 and 2.2 introduce the basic ion chemistry. Section 2.3 provides parameterizations for proton hydrate reaction rates, thus allowing us to incorporate heavy clusters into the ion-chemical scheme. The possible growth of these clusters to condensation nuclei for ice particles is introduced in section 2.4. Finally, section 2.5 describes Natanson's charge capture formalism that is used to treat both cluster / electron recombination and ice particle / charge interaction. Chapter 3 presents simulation results that illustrate these various model features. Chapter 4 discusses these results with regard to the summer mesopause environment. In 4.1, results are compared to in situ charge measurements in the vicinity of ice particles. Section 4.2 investigates particle effects on the ion composition, while sections 4.3 and 4.4 discuss implications for ionic nucleation. Conclusions are given in chapter 5.

When dealing with ion chemistry in the polar summer mesosphere, it has to be kept in mind that many conclusions must remain qualitative. Several complications arise under these cold conditions (T < 150 K): Many reaction coefficients are highly uncertain at these temperatures or rely only on extrapolations; proton hydrates can grow to large sizes for which reaction rates have not been measured; the capture of electrons and ions by ice particles complicates the reaction scheme. In particular, clustering simulations must currently rely on interpolations between kinetic (molecular ion) and thermodynamic (ice particle) approximations. Given these quantitative limitations, many basic conclusions can still be drawn about mechanisms in the mesospheric dusty plasma.

2. Model

2.1. Ionization sources

The neutral atmospheric input for OASIS can be taken from MSISE-90 [Hedin, 1991] or from individual data sets. The input used for the present work is discussed in section 3. Figure 1 shows typical profiles of ionization in the summer mesopause region. The solar zenith angle corresponds to mid-July at 67.9°N, Figure 1a represents quiet twilight conditions at local midnight (χ = 91°). Figures 1b and c refer to local noon (χ = 47°) under geomagnetically quiet and active conditions, respectively. (Twilight conditions are important since they are typical for many NLC observations and in situ experiments.) During daytime, the major continuous source of charge in the mesopause region is solar EUV radiation, in particular Lyman-α ionization of NO. Galactic cosmic rays become important below 80 km. During geomagnetically perturbed conditions, electron and proton precipitation can increase ionization rates in the NLC/PMSE region by several orders of magnitude. The ionization profile in Figure 1c corresponds to a precipitating electron flux of 10^{-7} J cm^{-2} s^{-1} distributed over a Maxwellian energy spectrum with a characteristic energy of 10 keV. Major products of ionization by precipitating particles are N_2^+, N^+, O_2^+ and O^+, which at
mesospheric altitudes are rapidly converted into the "primary ions" \( \text{O}_2^+ \) and \( \text{NO}^+ \). During twilight and at night in the absence of particle precipitation, ionization of NO by geocoronal Lyman-\(\alpha\) dominates the charge production at NLC/PMSE altitudes.

As solar input for photoionization we use the spectra given by Torr and Torr [1985] for high and low solar activity, extended towards longer wavelength with spectrum R74113 by Heroux and Hinteregger [1978]. We interpolate these spectra linearly with solar activity in accordance with the F10.7 flux extended towards longer wavelength with spectrum R74113 by the current work. Solar Lyman-\(\alpha\) is interpolated in the same way [Brasseur and Solomon, 1986] or taken from direct measurements [e.g., Lean, 1987]. Absorbing species in the model are \( \text{N}_2 \), \( \text{O}_2 \), O, NO, \( \text{O}_3(\Delta \lambda) \), and \( \text{CO}_2 \). The transfer of direct solar radiation is calculated for a spherical atmosphere; absorption and photoionization cross section are used as tabulated by Turunen et al. [1996]. The photon flux of geocoronal Lyman-\(\alpha\) is based on measurements by Meier and Mange [1973]. A parameterization as a function of solar zenith angle has been given by Strobel et al. [1974] with extrapolations to lower altitudes by Thomas and Bowman [1985a].

The role of energetic particle precipitation in mesospheric ionization has discussed e.g. by Rusch et al. [1981] and Frahm et al. [1997]. We describe the energy deposition and ionization using the formalism of Rees [1969; 1982], which has been extended to lower altitudes by Kirkwood and Osepian [1995]. Maxwellian and Gaussian energy spectra are used to represent diffuse and discrete auroral conditions, respectively [Strickland et al., 1983]. Alternatively, measured energy spectra can be used as input [e.g., Rapp et al., 2002a]. Ionization by galactic cosmic rays (GCR) is parameterized according to Heaps [1978] with the branching ratios for the individual ions given by Rusch et al. [1981].

### 2.2. Ion Chemistry

OASIS is a one-dimensional steady state model for the ion-chemistry of the D-region. As ion-chemical lifetimes are generally short, transport processes are not considered. Under the conditions of interest, reaction time constants for initial clustering and successive proton hydrate growth are of the order of seconds and milliseconds, respectively. Transport times over a vertical distance of 1 km by advection or diffusion are typically several hours [Brasseur and Solomon, 1984]. The numerical scheme for the steady state equations builds on the Newton-Raphson method, considering overall charge neutrality. Simulations typically comprise 25 ions and an additional arbitrary number of proton hydrates. The basic OASIS ideas are similar to other D-region ion models [Reid, 1976; Kopp, 1996; Turunen et al., 1996], and we refer to these publications for more general discussions of the chemistry.

Reaction rate coefficients have largely been taken from the compilation by Kopp [1996]; rates for the clustering processes are discussed in the next section. Figure 2 shows the basic positive ion reaction scheme. In order to illustrate the role of individual reaction paths, the thickness of the arrows resembles the individual rates. The rates correspond to quiet daytime conditions (Figures 1b, 4, 5b).

In the mesosphere, primary ions are efficiently transformed into proton hydrates. Starting out from \( \text{O}_2^+ \) and \( \text{NO}^+ \), there are two distinct reaction chains. Both are complex and indirect; they involve three-body clustering with major neutral constituents and fast two-body switching reactions of the intermediates [Chakrabarty et al., 1978; Reid, 1989]. The \( \text{O}_2^+ \) chain was identified by Fehsenfeld and Ferguson [1969] and Good et al. [1970]. The initial step that determines the overall time constant is the formation of \( \text{O}_3^+ \). Subsequent switching reactions lead to the first proton hydrates. Efficient hydration in the \( \text{NO}^+ \) chain involves intermediate clusters with the more abundant species \( \text{N}_2 \) and \( \text{CO}_2 \) rather than direct clustering with \( \text{H}_2\text{O} \) [Ferguson, 1971]. A final switching step leads to the third proton hydrate. Only for \( n > 3 \) is the direct hydration of \( \text{H}^+(\text{H}_2\text{O})_n \) thought to dominate over indirect reactions via intermediates with \( \text{CO}_2 \) or \( \text{N}_2 \) [Chakrabarty et al., 1978]. Considering the ionization sources, the \( \text{NO}^+ \) chain is always important, while the \( \text{O}_2^+ \) chain only gains a significant role under perturbed conditions.

Proton hydrates largely govern the positive ion composition below about 80-85 km. The above scheme of initial clustering steps gives rise to a sharp decline in the proton hydrate abundance above these altitudes. Several factors contribute to this abrupt change: the need for three-body reactions, the decline in water availability and enhanced recombination connected to a ledge in the electron number density. Laboratory data about proton hydrate reactions is available only to about \( n = 6 \). The clustering to larger sizes will be discussed in the next section.

The current version of the OASIS model uses only a very crude scheme for negative ions. Only two species are simulated: \( \text{O}_7^- \) and \( \text{X}^- \), the latter representing "heavy negative ions" [Torkar and Friedrich, 1983]. This is justified for simulations of the summer mesopause region since contributions of negative ions to the charge budget are negligible above 80 km under most conditions [Thomas and Bowman, 1985b]. Neither does the current OASIS model include metallic ions [e.g., Plane, 1991]. These ions are usually rapidly depleted below 95 km [Kopp, 1997], due to conversion to molecular ions and subsequent efficient recombination [Plane et al., 1999]. Their chemistry is not expected to be involved in the growth of proton hydrates. On the other hand, Goldberg and Witt [1977] found families of \( \text{Fe}^2 \) hydrate clusters during mass spectrometric measurements in NLC conditions.

OASIS does not comprise any feedback on the neutral chemistry. Effects of ionization on the abundance of NO and OH, and indirectly on \( \text{O}_3 \), have been discussed e.g. by Rusch et al. [1981] and Jackman et al. [1990]. As Lyman-\(\alpha\) ionization of NO is an important source of ions, the ion-chemical production of NO will be incorporated into future versions of OASIS. However, the local feedback of NO production on ionization rates may not be large: Ion-chemical production of NO is restricted to conditions of energetic particle precipitation. Ionization of NO by Lyman-\(\alpha\), on the other hand, plays a dominant role only under geomagnetically quiet conditions.
Mesospheric ion-chemistry is complex. Many reaction rates are uncertain or based solely on estimates. The latter applies e.g. to many reactions involving intermediate clusters in the NO$^+$ chain that were originally suggested by Reid [1977] and that are frequently used in current models. Other reactions are still controversial. An example is the conversion of the primary ions

$$\text{O}_3^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$$

that has been suggested with a rate coefficient of $5 \times 10^{-16}$ cm$^3$ s$^{-1}$ [Rees, 1989], which would have a significant impact on auroral production of NO. However, a laboratory measurement by Matsuoka et al. [1981] failed to observe NO$^+$ production associated with the decay of O$_3^+$ and thus placed an upper limit of $2 \times 10^{-18}$ cm$^3$ s$^{-1}$. This low rate would render reaction 1 insignificant for atmospheric applications. A more comprehensive discussion of critical reaction rates and a comparison to D-region mass spectrometer measurements will be published elsewhere.

Uncertainties are particularly serious for cold summer mesopause conditions because of enhanced clustering processes and limited knowledge about the temperature dependence of many reactions. The large number of interdependent reactions also complicates comparisons of model results with atmospheric measurements such as radar or in situ mass spectrometry. In particular, it is difficult to draw unambiguous conclusions about individual rate coefficients from these measurements. These limitations need to be kept in mind and many conclusions must remain qualitative.

### 2.3. Cluster Growth

Under most mesospheric conditions, the number of ligands in proton hydrates does not exceed $n = 4$-$6$. However, near the cold polar summer mesopause, growth to larger clusters is possible [Yang and Castleman, 1991]. Available in situ measurements cover the range up to $n = 21$ [Björn and Arnold, 1981].

In thermodynamical terms, hydration processes are governed by the Gibbs free energy of cluster growth [Castleman and Tang, 1972]. Homogeneous nucleation of ice particles is not feasible in the mesosphere as it exhibits a Gibbs free energy barrier that cannot be overcome [Witt, 1969]. This is illustrated for specific conditions by the dashed curves in Figure 3. When growth takes place about an ion, Coulomb interaction lowers the barrier, or completely removes it at sufficiently high supersaturation [Castleman et al., 1978], as shown by the solid curves in Figure 3.

Equivalently to the thermodynamic picture, cluster growth can be described in terms of reaction kinetics by a balance between the forward clustering reaction

$$\text{H}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}^+(\text{H}_2\text{O})_n + \text{M}$$

and the unimolecular decomposition

$$\text{H}^+(\text{H}_2\text{O})_n + \text{M} \rightarrow \text{H}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} + \text{M}.$$  

Applying detailed balancing, the reaction coefficients for forward reaction $k_f$ and backward reaction $k_b$ are related via the Gibbs free energy change $\Delta G_{n-1,n}$ of the corresponding clustering step [Castleman and Tang, 1972]:

$$
\frac{k_f}{k_b} \left[ \frac{\text{H}_2\text{O}}{\text{M}} \right] = \exp \left( -\frac{\Delta G_{n-1,n}}{kT} \right).
$$

In the present work, we apply the Thomson equation to describe the Gibbs free energy [e.g., Mason, 1971; Holland and Castleman, 1982]. Just as the Kelvin equation for homogeneous nucleation, the Thomson equation is based on a liquid drop formulation where the energetics of adding or removing molecules is treated in terms of surface energy (capillarity approximation). In this framework, the stepwise change of Gibbs free energy is given by

$$
\Delta G_{n-1,n} = -kT \ln \left( \frac{P_{\text{H}_2\text{O}}}{P_S} \right) + \frac{32\pi M^2}{3\rho_{\text{ice}} n} \sigma \left( \frac{1}{\varepsilon - 1} \right) \left( \frac{\rho_{\text{ice}}}{M} \right)^{1/3} \left( \frac{4\pi}{3n} \right)^{4/3}.
$$

Here, $P_{\text{H}_2\text{O}}$ is the ambient pressure of water vapor and $P_S$ is the saturation pressure above ice. $M$ is the mass of a water molecule, $\rho_{\text{ice}}$ the mass density of ice. $\sigma$ and $\varepsilon$ are the surface energy and dielectric constant of ice. The three terms in equation 5 describe energy changes connected to evaporation, surface area and electric field, respectively. Assuming a spherical droplet with the mass density of bulk ice, the radius of the $n$th cluster in equation 5 is

$$
r_n = \left( \frac{3M n}{4\pi \rho_{\text{ice}}} \right)^{1/3}.
$$

We have used the parameters given by Shi et al. [1993] for 130 K ($\rho_{\text{ice}} = 937$ kg m$^{-3}$, $\sigma = 0.00995$ J m$^{-2}$, $\varepsilon = 132$). The temperature-dependent saturation vapor pressure by Marti and Mauersberger [1993] is applied down to mesopause temperatures.

The use of the classical Thomson theory obviously is an approximation. Limitations of this approach have been discussed by Castleman et al. [1972; 1978] and Holland and Castleman [1982], Chan and Molzen [1980] have introduced corrections to the Thomson equation for small clusters. Sugiyama [1994] used the clustering formulation by Lothe and Pound [1962]. Ultimately, more laboratory measurements representative for mesospheric conditions will be needed to better quantify the role of proton hydrates at the summer mesopause.
\[ \Delta G_{0,n} = \sum_{1}^{n} \Delta G_{n-1,n} \]  

with the energy of the ionic nucleus normalized to zero. Atmospheric conditions resemble an altitude of 86 km with \( N_{\text{air}} = 2 \times 10^{14} \text{ cm}^{-3} \) and a water vapor mixing ratio of 3 ppm. The strong temperature dependence of the Gibbs free energy barrier is obvious. For the conditions in Figure 3, the barrier disappears at temperatures below about 130 K. At higher temperatures, there is a distinct minimum in the free energy curves that corresponds to the most abundant cluster sizes under those conditions. Also shown in Figure 3 are the significantly larger Gibbs free energy barriers for homogeneous nucleation, i.e. cluster growth about a neutral water molecule \([\text{Gadsden and Schröder, 1989}].\)  

Equation 4 defines the relative rates of forward and backward reactions in the cluster chain. These equilibrium considerations have been applied e.g. by D'Auria and Turco \([2001] \) to study the size distribution of proton hydrates in the stratosphere. They find size distributions peaking at \( n = 6-14 \) in the temperature range 220-170 K.  

However, in the mesosphere this equilibrium between 2 and 3 is no longer valid because the growth process must compete with the termination of the clustering chain by efficient recombination with free electrons  

\[ \text{H}^+(\text{H}_2\text{O})_n + \text{e}^- \rightarrow \text{neutral products} \]  

Consequently, in order to determine cluster size distributions in the D-region, it is not sufficient to know the relative rates of reactions 2 and 3 as determined by detailed balancing. Rather, absolute rate coefficients for clustering and recombination are needed together with the local production rate of ions and electrons. This is a serious limitation for mesospheric cluster studies. Clustering rates have been measured in the laboratory only up to \( n = 6 \) \([\text{Lau et al., 1982} \), restricted to \( \text{CH}_4 \) as third body and to temperatures above 200 K. At lower temperatures, these measurements indicate that the forward step 2 can be described as a quasi 2nd order reaction in \( \text{H}^+(\text{H}_2\text{O})_n \) and \( \text{H}_2\text{O} \), independent of the third body density \([\text{Lau et al., 1982; Yang and Castileman, 1991}].\) We follow the approach of Sugiyama \([1994] \) and adopt a Langevin rate of \( 1 \times 10^{9} \text{ cm}^3 \text{ s}^{-1} \) for the clustering step \([\text{Chesnavich et al., 1980}].\) The backward rate is then obtained by detailed balancing.  

Also laboratory results on recombination coefficients (reaction 8) are available only up to \( n = 6 \) and at temperatures above 200 K \([\text{Leu et al., 1973; Huang et al., 1978; Johnsen, 1993}].\) Sugiyama \([1994] \) has extended these rates to larger sizes by assuming a size-independent recombination coefficient \( \alpha_n = 5 \times 10^{-6} \sqrt{300/T} \text{ cm}^3 \text{ s}^{-1} \). In the present work, we deem a size-dependent recombination efficiency to be a more realistic approach. In the limit of large clusters, the coefficient should merge the result for ice particles. Therefore, we apply the particle / charge capture formulation by Natanson \([1960] \) to cluster reaction 8 (see section 2.5). Resulting recombination rates increase with \( n^{1.3} \). As discussed in section 4.1, these rates generally exceed Sugiyama’s values.  

Considering the number of steps necessary for the production of large hydrates, the extreme sensitivity of the clustering process to temperature, water abundance and electron density becomes evident: At each individual clustering step, the water density enters into the forward direction and the temperature via the Gibbs free energy into the backward direction. Also at each step, recombination threatens to terminate the entire clustering chain. At temperatures around 130 K, reaction 2 and 3 are in a rough balance and the clustering process is mathematically similar to a "diffusion" in \( n \)-space. At lower temperatures, the backward reaction loses importance and the growth process can be regarded as an "advection" towards larger \( n \), limited only by the recombination reaction.  

### 2.4. Ionic Nucleation  

Two major candidates have been suggested to act as embryos for ice particle nucleation near the mesopause: meteoric material and cluster ions. As discussed in the introduction, it is today widely assumed that meteoric smoke particles are the dominant condensation nuclei in the mesosphere \([\text{Turco et al., 1982; Keesee, 1989}].\) In the OASIS model, we have incorporated the generation of ionic condensation nuclei as a direct extension of the cluster growth parameterization. This allows us to study the feasibility of ionic contributions to nucleation under various mesopause conditions. Arnold \([1980] \) has described the growth of ice particles on proton hydrates, and a detailed mechanism has been outlined by Sugiyama \([1994] \). As discussed in the previous section, the Gibbs free energy barrier for ionic nucleation vanishes at sufficiently low temperature (solid curves in Figure 3). However, this does imply a run-away particle growth. Rather, the growth of the ion clusters has to compete with efficient recombination reaction 8. Hence, a stable ice particle can only be nucleated if the neutral particle produced during recombination is beyond the Gibbs free energy barrier for neutral particles (dashed curves in Figure 3).  

Upon recombination, energy is released that needs to be dissipated by sublimation of individual water molecules from the cluster. Sugiyama \([1994] \) suggested that 13.6 eV need to be dissipated, which would require the sublimation of about 30 molecules. Hence, smaller clusters would be completely destroyed by the recombination. However, while 13.6 eV is the energy released by recombination of a free \( \text{H}^+ \), significantly less energy is released when a solvated proton recombines. Hence, the sublimation of as many as 30 molecules upon cluster recombination as suggested by Sugiyama \([1994] \) has to be regarded as an upper limit. Nevertheless, we use this number of 30 molecules in our model in order to arrive at a conservative estimate of ionic nucleation efficiencies. The above scheme defines a critical cluster size for ionic nucleation: a proton hydrate must grow to a size of about 30 molecules above the neutral Gibbs free energy barrier before it can successfully act as a condensation nucleus.  

As can be expected from the discussion about clustering in the previous section, the feasibility of ionic nucleation is extremely sensitive to atmospheric conditions \([\text{Sugiyama, 1994}].\) Gumbel and Witt \([2002] \) have discussed the
implementation of Sugiyama’s nucleation scheme into the OASIS model. For most mesospheric conditions, the critical proton hydrate size is beyond 100. The OASIS output comprises this critical size as well as the corresponding nucleation rate \( J \), which is equal to the rate of proton hydrates reaching this critical size.

2.5. Charge Capture

In the OASIS model, parameterization of charge capture is used in two connections: One is the recombination of proton hydrate clusters with electrons discussed in section 2.3. The other is the capture of charge by ice particles.

The capture of electrons or ions by aerosol particles has been described by Natanson [1960]. Analytical approximations for mesospheric conditions have been obtained by Rapp [2000]. Capture rates are essentially determined by the cross section of the particle, the thermal speed of the electron or ion and an additional term describing the Coulomb interaction. The capture rate of electrons or singly charged ions by a neutral particle of radius \( r \) is

\[
k_0 = \pi r^2 \bar{c} \left( 1 + \frac{e^2}{8\varepsilon_0 kT \bar{c} r} \right)
\]

(9)

with the mean thermal speed of the electron or ion

\[
\bar{c} = \sqrt{\frac{8kT}{\mu m}}.
\]

(10)

This dependence on the thermal speed obviously makes the capture of electrons a much more efficient process than the capture of ions. The attractive capture of an electron or ion by an oppositely charged particle with charge number \( q \) and radius \( r \) is

\[
k_a = \pi r^2 \bar{c} \left( 1 + \frac{|q| e^2}{4\pi \varepsilon_0 kT \bar{c} r} \right).
\]

(11)

The current version of the model handles only singly charged particles. This is reasonable for particle radii up to about 10 nm since multiple charging only becomes feasible for larger particles [Rapp and Lübken, 1999]. The current model does not include photodetachment of electrons from the ice particles.

3. Results

3.1. Ion Composition

Simulations in this paper were performed for mid-July conditions at 67.9°N. Figure 4 shows the neutral atmospheric input. A temperature profile was taken from the high-latitude climatology of Lübken [1999] with a minimum of 129.5 K at 88 km. The NRL CHEM2D model [Summers et al., 1997] provided a water profile featuring a mixing ratio of 3 ppm at 86 km. A representative NO profile was obtained from UARS / HALOE measurements [Siskind et al., 1998]. Odd oxygen species were taken from NLC-related in situ measurements by Gumbel et al. [1998].

Figure 5 shows resulting ion profiles corresponding to the ionization conditions in Figure 1. Cluster ions have been summarized in groups. The “intermediate” profile comprises all intermediate clusters. Two characteristic altitudes can be identified: the transition from NO³/O³⁺ dominance to intermediate clusters, and the transition from intermediate clusters to proton hydrates. Both altitudes are considerably higher in the polar summer mesosphere than during other (warmer) conditions. However, these transitions decrease in altitude with increasing ionization. For the examples in Figure 5, the primary/intermediate transition is at 92, 91, and 85 km, while the intermediate/hydrate transition decreases takes place at 88, 85, and 84 km for twilight, daytime, and perturbed conditions, respectively.

Generally, the overall number of ion species increases with increasing ionization. However, this is not true for the larger proton hydrates (\( n > 10 \)). The reason is the larger recombination coefficient of these clusters. This causes the increased clustering from smaller ions to be more than compensated by destructive recombination with the enhanced electrons. This is also evident from the detailed cluster distributions in Figure 6. Shown are the cluster spectra at 86 km for the three cases in Figure 5. While the small proton hydrates correlate with the ionization just as the small ions, this trend reverses for the larger proton hydrates. In section 3.3, the influence of ionization on the growth towards even larger clusters and ice particles at lower temperatures will be discussed.

3.2. Particle Effects

The impact of ice particles on the abundance of electrons and ions has been studied e.g. by Reid [1990] and Rapp and Lübken [2001]. With the OASIS model we have now the possibility to look at particle effects on the detailed ion composition. As an example, particle layers extending from 84 to 87 km have been introduced to the twilight conditions and perturbed conditions in Figure 5a and c. We adopt a small (2×10² cm⁻³) and a large (2×10⁷ cm⁻³) population of particles with radius 5 nm. Applying these particles to conditions of low and high ionization (Figure 1a, c), some limiting cases of particle effects can be studied.

In quiet twilight conditions with few particles (Figure 7a), the particles cause a moderate bite-out in the electron density. Nearly all particles carry negative charge. As the electron density decreases, so does the recombination rate. This causes an enhancement of the proton hydrate density. With 2×10⁵ cm⁻³ particles (Figure 7b), a huge electron bite-out is caused. Given the large surplus of particles, now also the capture of ions becomes efficient, and the proton hydrates are depleted as well. Almost all charge is carried by the particles; there are about equal numbers of positive and negative particles. Nevertheless, most particles remain neutral. As compared to the no-particle situation, the local charge density has increased by more than an order of magnitude.
In the case of high ionization rates (Figure 8a, b), the particle layers can cause only moderate depletions of the electron density. Almost all particles become negatively charged. And again, reduced recombination leads to an enhancement in the proton hydrate densities.

Our findings are generally consistent with the charts given by Rapp and Lübken [2001] that describe charging conditions as a function of particle population and ionization. As a new feature, the OASIS model can provide detailed insight into the fate of individual ion and cluster species. Situations with both enhancement and bit-outs in the ion profile have been observed in situ in connection with ice particle layers [e.g., Lübken and Rapp, 2001] and will be discussed further in section 4.1. Jensen and Thomas [1991] and Reid [1997] have discussed the influence of particle charging on coagulation processes. The situation in Figure 7b will enhance coagulation by Coulomb attraction between positive and negative ice particles. However, as in most mesospheric conditions negative charge completely dominates the particle population, coagulation processes in NLC and PMSE will usually be suppressed by Coulomb repulsion.

It is important to consider the lifetime of particle charges against recombination. This is highly dependent on the ionization conditions. Ignoring possible contributions of photodetachment processes, the lifetime of negatively charged particles at 86 km in Figure 7 is several hours. This is critical in terms of the steady state assumption, in particular when considering sedimentation transport of the ice particles. For the high-ionization conditions in Figure 8, on the other hand, the lifetime of the negative particle charges reduces to tens of seconds. This is short as compared to local transport processes. In this situation, the concept of charged particles and their role in mesopause phenomena must be considered as a fairly dynamic rather than as a static idea.

3.3. Clustering and Nucleation

As pointed out in sections 2.3 and 2.4, cluster growth and the feasibility of ionic nucleation depend strongly on atmospheric conditions. Corresponding examples of OASIS output are shown in Figure 9. Black lines denote cluster spectra representative for about 86 km at quiet daytime conditions (Figure 1b, $Q = 10 \text{ cm}^{-3} \text{ s}^{-1}$, $N_{\text{al}} = 2 \times 10^{14} \text{ cm}^{-3}$, 3 ppm water vapor) at various temperatures. As the temperature decreases, the balance of the proton hydrate reactions (equation 4) changes rapidly and gives rise to a strongly enhanced clustering process. At 128 K, significant cluster concentrations are found beyond the critical proton hydrate size for nucleation ($n = 73$) under these conditions. The ionic nucleation rate $J$, i.e. the production rate of proton hydrates of this critical size, is $0.2 \text{ cm}^{-3} \text{ s}^{-1}$. In other words, 2% of all ions originally produced ultimately are converted into ice condensation nuclei.

Capture of electrons by ice particles can enhance the clustering process. This is shown by the gray curves in Figure 9. These curves represent cluster spectra under the same conditions as above, but with a population of $10^3 \text{ cm}^{-3}$ particles of radius 10 nm added. The resulting decline in recombination leads to a strong increase of the larger clusters. The nucleation rate at 128 K increases to $1.5 \text{ cm}^{-3} \text{ s}^{-1}$, i.e. the ionic nucleation efficiency becomes 15%. This feedback of existing particles on the nucleation of new particles has been discussed by Gunbel and Witt [2002] and will be considered further in section 4.3.

4. Discussion

4.1. In Situ and Model Results

Figures 7 and 8 cover a wide range of ionospheric conditions near the mesopause. In the presence of particles, we generally find bite-outs in the electron density profiles. For the less mobile positive ions, the picture is more complex as two effects compete in the presence of particles: capture by particles tends to reduce the ion density while the diminished electron population leads to reduced recombination, which tends to enhance the positive ions. Our results suggest that the latter effect is dominant under most conditions. Ion bite-outs are only to be expected under conditions of relatively low ionization with large numbers of particles present.

The OASIS results are in general agreement with the findings by Rapp and Lübken [2001]. In a comprehensive study on particle charging, these authors find that indeed almost all combinations of electron biteouts and ion depletions/enhancements are achievable in the D-region depending on particle population and ionospheric conditions like ionization rate and recombination rate. Rapp and Lübken [2001] show specifically that ion enhancements in the presence of particles are most likely to occur when the ion population exhibits heavy clusters (i.e., large effective recombination coefficients). In the OASIS model, this effective recombination coefficient is no longer a free parameter but follows directly from the simulated ion composition (see section 4.2).

A number of simultaneous in situ charge and particle measurements are available in the summer mesosphere, as reviewed by Lübken and Rapp [2001]. Detailed ion composition measurements are available of rocket-borne ion mass spectrometers flown by the Max-Planck-Institut für Kernphysik, Germany [e.g., Björn and Arnold, 1981], the University of Bern, Switzerland [e.g., Balsiger et al., 1996], and NASA Goddard Space Flight Center [Goldberg and Witt, 1977]. In addition, measurements by positive ion probes can give a coarse picture of particle influences on ion chemistry without revealing details of the ion composition [e.g., Blix and Thrane, 1993]. However, comparisons of model results to these measurements are difficult. Some caveats are listed here: Information about the particle population is usually restricted to their pure existence (NLC, PMSE) and does not reveal necessary details about number density or size distribution. Also, particles are usually not restricted to optically observed layers, but may be present in the form of sub-visible, possibly persistent populations throughout the summer mesopause region [von Zahn and Berger, 2002]. As opposed to model simulations, in situ measurements obviously cannot allow for a direct comparison of particle / no particle conditions. Hence, the interpretation of measured structures in ion / electron profiles often remains ambiguous in terms of the role of
particles or other processes like local dynamics. A limitation of many mass spectrometer measurements is the limited mass range (e.g., n < 10) as the behavior of smaller proton hydrates is not necessarily representative for the entire cluster population (Figures 6 and 9). Finally, temperature information in the region is usually not available with sufficient altitude resolution and accuracy.

Keeping these limitations in mind, a review of the data collected by Lübken and Rapp [2001] reveals that electron bite-outs are indeed a common phenomenon in connection with NLC and PMSE. However, the data show that ion enhancements are relatively scarce under the same conditions. Ten of the flights reviewed by Lübken and Rapp [2001] had the capability to measure profiles of positive ions. Only two measurements of these, both by electrostatic ion probes, reveal clear ion enhancements [Blix and Thrane, 1993; Blix, 1999]. In addition, the mass spectrometer measurement by Balsiger et al. [1993] shows a narrow layer of enhanced proton hydrates while the total positive ion density is depleted. Mass spectrometer data presented by Kopp et al. [1985] (flight S26/1) feature a broad layer of reduced electron densities at 80-90 km. A broad maximum of proton hydrate densities over the same height range may be indicative of an enhancement due to reduced recombination. On the other hand, ion depletions are clearly observed on five flights [Pedersen et al., 1969; Johannessen and Kranzowski, 1972; Balsiger et al., 1993; 1996; Blix, 1999]. These observations range from very low (Q ≈ 0.006 cm^{-3} s^{-1}) to moderate (Q = 400 cm^{-3} s^{-1}) ionization conditions. This predominance of ion depletion in connection with NLC or PMSE is seemingly in contrast with the model results in section 3.2. The model simulations suggest for most mesospheric conditions a tendency of ion enhancement due to electron capture and reduced recombination in the presence of ice particles. A possible explanation of the depletions is a presence of populations of very many (small) particles. This has also been suggested by Balsiger et al. [1996] for the case of their ion depletion measurement. It is interesting that the existence of large amounts of particles has also been pointed out by Rapp et al. [2001a] as a possible explanation for the occurrence of PMSE up to very high ionization rates.

Some flight results are particularly interesting. Among the measurements listed above, the strongest ion depletion [Balsiger et al., 1996] and the clearest ion enhancement [Blix, 1999; Lübken and Rapp, 2001] in the presence of NLC were observed only 39 minutes apart within the same rocket salvo (NLC-93, Esrange, Sweden). Both flights took place under very quiet twilight conditions. The substantial difference in the particle effect on the positive ions points to the presence of very different local particle populations during these two flights, resulting in conditions as resembled in Figures 7a and b. Kopp et al. [1984] presented mass spectrometer data obtained during a simultaneous NLC and aurora event with very high ionization rates (Q = 6000 cm^{-3} s^{-1}). For this flight, no obvious depletions or enhancements were observed in the particle layer, neither for the electrons nor for the positive ions. This small effect is consistent with model results for high ionization and small particle populations (Figure 8a). Finally, Havnes et al. [1996] presented particle and electron measurements in NLC/PMSE that showed a dominant population of positively charged particles together with an enhancement in the electron profile. These observations cannot be explained in the framework of the present particle charging model. It has been suggested that the photoeffect acting on ice particles that contain metallic impurities is a source of large positive particle charges. However, Rapp and Lübken [1999] showed that this mechanism is not feasible in the mesopause environment. The generation of positive particle populations remains an open issue.

### 4.2. Effects of Heavy Clusters

Clustering processes have significant influence on charge mobility in the mesopause region. Heavy charge carriers have frequently been measured in situ by rocket-borne Gerden condensers [e.g., Croskey et al., 2001]. It is commonly accepted that the reduction of charge mobility by ambipolar interaction with charged particles is a crucial ingredient of PMSE [Cho et al., 1992]. The results of the present work suggest that the effect of particles on charge mobility is twofold: In addition to direct ambipolar forces on the electrons, the particles can reduce the mobility in the plasma further by enhancing the growth of positive charge carriers to significantly larger cluster sizes (Figure 9).

Cluster growth also has a strong effect on the overall recombination rate. Figure 10 shows recombination coefficients for the proton hydrates. Laboratory measurements for n ≤ 6 have been scaled from the laboratory results to 130 K using a T^{−1/2} dependence. The recombination parameterization used in the present work [Natanson, 1960] is compared to the value applied by Sugiyama [1994]. The use of more efficient recombination in our simulations yields more conservative estimates for the efficiencies of ion clustering and particle nucleation.

Above 80 km, the effective recombination coefficient can be defined as

\[ \alpha_{\text{eff}} = \sum_i N_i \alpha_i, \]  

(13)

where \( N_i \) and \( \alpha_i \) are individual number densities and recombination coefficients and \( i \) sums over all positive ion species. (Below 80 km, a similar definition needs to take into account contributions of negative ions [e.g., Montbriand and Belrose, 1981].) \( \alpha_{\text{eff}} \) is an important parameter for the assessment of D-region processes. It is applied e.g. in the analysis of radar measurements in order to relate electron densities and ion production rates [e.g., Hargreaves et al., 1987; Kirkwood and Osepian, 1995]. It is also used in particle charging models [e.g., Reid, 1990; Rapp and Lübken, 2001] and in ion-chemical models that do not attempt to simulate the entire set of mesospheric ion species [e.g., Rodriguez and Inan, 1994; Rodger et al., 1998]. In steady state conditions, the local electron number density \( N_e \) in the mesopause region is determined by a balance between ion production rate \( Q \) and the recombination of ions and electrons.
The lifetime of electrons against recombination is determined by the same parameters as

$$\tau_e = \frac{1}{\sqrt{Q \alpha_{\text{eff}}}}.$$  \hfill (15)

While equation 14 formally provides a simple relationship between charge production and charge density, any application to atmospheric problems is limited by the knowledge of $\alpha_{\text{eff}}$ [Gledhill, 1986]. Individual recombination coefficients vary from a few $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for light molecular ions to several $10^{-5}$ cm$^3$ s$^{-1}$ for proton hydrates (Figure 10). As a consequence, detailed information about ion composition and, hence, about ion chemistry is needed in order to access $\alpha_{\text{eff}}$. This is in particular true in the summer mesopause region where cluster formation in local temperature minima can push $\alpha_{\text{eff}}$ to very large values. The OASIS model can provide parameterizations of $\alpha_{\text{eff}}$ as a function of D-region conditions and particle abundance.

### 4.3. Ionic Nucleation and Layered Structures

Based on currently available laboratory data on cluster growth, we deem ionic nucleation not to be feasible under average conditions near the high-latitude summer mesopause. However, conditions required for ionic nucleation are within the range of mesopause variability. Figure 11 summarizes the feasibility of ionic nucleation as a function of the critical parameters temperature, water abundance and ionization. Each curve in the figure is representative for a specific water concentration (0.3, 1, 3, 10, or 30 ppm). The area to the left of a given curve specifies the range of temperature and ionization that make ionic nucleation for this given water concentration efficient. As "efficient" we have considered ionic nucleation rates that exceed a threshold of $J_0 = 0.03 \text{ cm}^3 \text{ s}^{-1}$. This corresponds to the nucleation of about 100 cm$^3$ ice particles per hour, which can be regarded as a reasonable value necessary for particle phenomena at the mesopause. Figure 11 is representative for an altitude of about 86 km ($N_{\text{eff}} = 2 \times 10^{14} \text{ cm}^{-3}$).

As discussed earlier by Turco et al. [1982] and Sugiyama [1994], Figure 11 shows a dramatic sensitivity of ionic nucleation to moderate changes in temperature or water abundance. As for the dependence of the ionization rate, for a given temperature and water abundance, there is a lower limit of $Q = J_0$, below which ionic nucleation cannot be feasible. This is obviously due to the fact that the number of nucleations cannot exceed the number of ions produced in the first place (nucleation efficiency 100%). An upper limit exists since increasing ionization leads to excessive electron concentrations and recombination, thus causing a termination of the cluster growth before the critical size is reached. For a temperature of 128 K and a water abundance of 3 ppm, limiting ionization rates of 0.1 and 1000 cm$^3$ s$^{-1}$ correspond to electron densities of about 100 and $2 \times 10^4$ cm$^{-3}$, respectively. It is interesting to compare this to a recent analysis of the range of electron densities over which PMSE can be observed. Rapp et al. [2002a] find a lower limit of 300-500 cm$^{-3}$ needed for the detection of PMSE with currently available radar sensitivities. An upper limit is reported at about $10^5$ cm$^{-3}$, presumably caused by the availability of ice particles needed to reduce the electron mobility.

Figures 9 and 11 show that small atmospheric variations in temperature or water abundance can have dramatic effects on ionic nucleation efficiencies. Ionic nucleation can become feasible given relatively small deviations from average conditions in the mesopause region as induced e.g. by gravity waves. As an example, we can consider a mean condition with a local temperature minimum of 130 K and a water abundance of 3 ppm. We let a gravity wave of amplitude 5 K pass. In the resulting minimum of 125 K, rapid cluster growth and ionic nucleation of ice particles will proceed. (Note that a proton hydrate with 100 ligands already corresponds to a particle of about 1 nm in radius.) At a later stage the temperature maximum of 135 K will pass. This will not destroy the newly generated particles since they are stable once growth has proceeded beyond the Gibbs free energy barrier corresponding to this temperature (compare Figure 3). Efficient generation of large proton hydrates in gravity waves has also been suggested by Hall [1990]. However, that description did not incorporate the role of the clusters as condensation nuclei and, as a consequence, the heavy clusters were destroyed again after the passage of the cold part of the wave. If, as in the present model, one allows for particle nucleation, the passage of a single wave period can cause a permanent change in the layer.

As already pointed out by Turco et al. [1982], it is important to note that ionic nucleation is fast once atmospheric conditions are sufficient. Typical reaction time constants for the initial clustering steps and the subsequent proton hydrate growth are of the order of seconds and milliseconds, respectively. Hence, temperature structures can “immediately” be converted into corresponding layers of small ice particles. Because of the extreme temperature dependence, temperature amplitudes of a few Kelvin can be sufficient to generate this particle layering. The persistency of the temperature minima together with the nucleation rate determines the total number of particles that can be nucleated at a given location. Distinct stratifications with sharp layers have been observed both in NLC and in the distribution of charged particles connected to PMSE [e.g., Havnes et al., 2001]. In order to study the atmospheric relationship between temperature structure and particle layering, simultaneous measurements with good spatial resolution are needed. Unfortunately, current climatologies of mesospheric temperatures must rely on measurement techniques of limited height resolution [e.g., Lübken, 1999]. All available in situ temperature measurements with sufficient height resolution (< 200 m) in the vicinity of NLC show multiple temperature minima in the mesopause region [Philbrick et al., 1984; Rapp et al., 2002b]. These measurements consistently find the visible cloud (i.e., the upper end of the particle size spectrum) in the lowermost minimum of these temperature profiles. On the other hand, it is important to note that a very efficient ionic generation of condensation nuclei can actually counteract the existence of...
visible clouds. As many particles compete for the available water vapor, average particle sizes may remain small and subvisible.

As Figure 11 shows, a critical limitation of this idea of rapid particle nucleation in local temperature minima is the availability of water vapor. A water abundance of 1 ppm or below would drastically reduce the feasibility of sufficient cluster growth. Although recent measurements and models predict higher abundances of water vapor in the upper mesosphere than previously assumed, freeze-drying is expected to significantly redistribute the water out of the NLC/PMSE region [Summers et al., 2001; von Zahn and Berger, 2002]. In a detailed assessment of the water budget, von Zahn and Berger [2002] predict a persistent dehydration of large parts of the region to water mixing ratios far below 1 ppm.

4.4. Feedback Mechanisms

We have outlined above how particles through electron capture can enhance the clustering process and, hence, ionic nucleation. This constitutes a positive feedback mechanism where the existence of ice particles boosts the nucleation of new ice particles. Gumbel and Witt [2002] have discussed this feedback in detail. They show that the presence of ice particles can extend the feasibility region in Figure 11 to significantly larger ionization rates and to slightly higher temperatures. This positive feedback has the potential of amplifying initial mesospheric structures e.g. in the ice particle population or in the electron density.

This is interesting for PMSE. A pre-condition for the presence of these echoes are structures in the electron density on the scale of the radar half wavelength (~meters) [Cho and Röttger, 1997]. Charging of ice particles is thought to provide the reduction of charge mobility that is necessary to maintain such small-scale structures [Cho et al., 1992]. However, it is still an open question how these structures can be generated in the first place. In this connection, a positive feedback mechanism is of obvious interest. However, Gumbel and Witt [2002] conclude that this feedback cannot be efficient enough to generate structures at such small scales as required for PMSE: In order to generate meter-scale structures, positive feedback processes must be fast enough to compete with the destruction of structures by particle diffusion. As a consequence, the order of 1000 cm\(^{-3}\) particles must be nucleated within minutes in order to provide a sufficiently fast feedback on the electron density [Gumbel and Witt, 2002]. This is not feasible under realistic mesospheric conditions.

Another potential ice particle feedback on cluster growth can be discussed. This is connected to the fate of atomic oxygen. The reaction

\[
\text{O}_4^+ + \text{O} \rightarrow \text{O}_2^+ + \text{O}_3 \tag{16}
\]

efficiently disrupts the initiating steps of the \(\text{O}_2^+\) clustering chain (Figure 2). It has thus been suggested that atomic oxygen clustering efficiencies may have a significant influence on the distribution of electrons and proton hydrates in the upper mesosphere [Fehsenfeld and Ferguson, 1972; Friedrich et al., 1999]. Moreover, \textit{in situ} measurements indicate that ice particles may act as a sink for atomic oxygen [Thomas, 1991; Gumbel et al., 1998]. Hence, a feedback scenario becomes possible where ice particles cause a biteout in the \(O\) density, which then enhances proton hydrate clustering and ionic nucleation by suppressing the termination reaction 16. We have studied this idea by reducing the \(O\) input profile (Figure 4) by a factor 10. Figure 12 shows that the effect on larger proton hydrates \((n > 10)\) remains minor. This is to be expected since reaction 16 does not have any major effect on the dominant \(NO^+\) cluster chain. We conclude that an ion-chemical feedback mechanism involving atomic oxygen capture is not feasible in the mesopause region. It should be noted, however, that while we do not find a strong influence of atomic oxygen near the mesopause, more significant effects are expected in the lower parts of the ionosphere where atomic oxygen is a major player in the negative ion chemistry [e.g., Thomas and Bowman, 1985b; Turunen et al., 1996].

5. Conclusions

The variety of mesospheric interactions involving charge requires combined studies of ions, clusters and particles. We have described an approach that includes these constituents in a single ion-chemical model. By parameterizing the growth of proton hydrates up to the sizes of ice condensation nuclei, the OASIS model for the first time bridges the ion-chemical gap between molecular ions and nanometer-sized particles. While describing the possibility of ionic nucleation, our model is not a complete particle growth model. Nevertheless, the ion-chemical features presented here can readily be coupled with existing NLC/PMSE models. This can be done either interactively or by providing parameterizations as a function of mesospheric conditions. Such parameterizations can describe effective recombination coefficients or effective ion masses, which are important quantities for simulations of particle charging [e.g., Rapp and Lübken, 2001]. Our detailed treatment of the clustering scheme can also provide improved parameterizations of ionic nucleation rates as a function of temperature, water abundance and background ionization (e.g., Figure 11). Many current NLC/PMSE models use parameterizations for ionic nucleation that do not directly involve the detailed ion chemistry behind the cluster growth [e.g., Turco et al., 1982; Sugiyama, 1994; Rapp et al., 2002b]. Other models do not allow for the option of ionic nucleation at all [e.g., Klöstermeyer, 1998; Berger and von Zahn, 2002].

As for the feasibility of ionic nucleation, we confirm earlier findings e.g. by Turco et al. [1982] and Keesee [1989] that clustering efficiencies are not sufficient under average mesospheric conditions. Hence, considering the wide range of conditions under which NLC and PMSE are observed, ionic nucleation is unlikely to serve as major nucleation mechanism in the mesopause region. In the competition between meteoric material and cluster ions as mesospheric condensation nuclei, strong freeze-drying is particularly critical for the ionic nucleation [von Zahn and Berger, 2002]. Nevertheless, we have shown that moderate deviations from the mean state may well shift conditions towards sufficient ionic nucleation efficiencies as defined in Figure 11. As a consequence, the
action of gravity waves can lead to rapid generation of particle layers in local temperature minima. Because of the extreme sensitivity of ionic nucleation on mesospheric parameters, stratifications of temperature or water abundance will result in steep vertical gradients of ionic particle generation. Very distinct particle layers are frequently observed both by optical and charged particle detection [e.g., Rapp et al., 2002b; Hovnes et al., 1996].

Major new results of the OASIS model concern the large impact of the presence of ice particles on ion chemistry and composition. As the particles efficiently capture electrons, ionic reactions, and in particular cluster growth, are less subject to termination by recombination. Hence, for most mesospheric conditions, we suggest an enhancement of positive ion densities in the presence of particles. Positive ion depletions, on the other hand, can generally be expected in situations when particle number densities exceed the undisturbed electron concentrations (Figures 7 and 8). These results are similar to model results e.g. by Reid [1990] and Rapp and Lübken [2001]. As compared to these models, the OASIS model has the advantage of inherently simulating quantities like the efficient recombination coefficient or the mean ion mass rather than introducing them as free parameters. In situ rocket data suggest that in a majority of simultaneous particle and charge measurements, depletions rather than enhancements of positive ions are found. This is seemingly in contrast to our model results. A possible explanation is the presence of populations with significantly more (smaller) particles than commonly assumed.

The enhancing effect of ice particles on cluster growth becomes most prominent when it comes to the possibility of ionic nucleation. Under appropriate mesospheric conditions, the presence of ice particles can strongly enhance the generation of ionic condensation nuclei for new particles. This was illustrated in Figure 9. This feedback mechanism has not been described in earlier mesospheric particle models. It has the potential of amplifying spatial fluctuations in the mesospheric dusty plasma. However, following the discussions by Gumbel and Witt [2002], we deem this particle/cluster/nucleation feedback not to be efficient enough to generate and maintain fluctuations on the small spatial scales needed for PMSE.

The above statements are based on currently available data on the kinetics and thermodynamics of ionic reactions and proton hydrate growth. Future laboratory studies of ionic-chemical reaction rates may readily shift these statements closer to or further away from feasibility. Laboratory studies under conditions representative for the cold summer mesopause are badly needed in order to clarify the role of ionic-chemical processes in the phenomena of this part of the atmosphere.

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Figure 1. Ionization profiles representative for high-latitude summer mesosphere conditions: (a) quiet twilight conditions, (b) quiet daytime conditions, (c) electron precipitation conditions.
Figure 2. Basic ion-chemistry scheme of the OASIS model. Arrow thicknesses represent reaction rates for quiet daytime conditions (Figure 1b). Not shown are recombination reactions with electrons.

Figure 3. Gibbs free energy of cluster / particle formation at different temperatures. Dashed lines denote homogeneous nucleation, solid lines denote growth about an ion nucleus. Atmospheric conditions are $N_{air} = 2 \times 10^{14}$ cm$^{-3}$ and a water vapor mixing ratio of 3 ppm.
Figure 4. Input profiles for temperature and neutral species. See text for references.

Figure 5. Ion composition profiles simulated for the ionization conditions in Figure 1 and the neutral atmosphere in Figure 4: (a) quiet twilight conditions, (b) quiet daytime conditions, (c) perturbed daytime conditions. The "intermediate" profile refers to the sum of all intermediate clusters.
**Figure 6.** Size spectra for the proton hydrates at 86 km for the three simulations in Figure 5.

**Figure 7.** Influence of ice particles on the ionospheric composition. The shaded area represents layers of (a) $2 \times 10^5$ and (b) $2 \times 10^4$ cm$^{-3}$ particles with radius 5 nm. Shown are electrons and total proton hydrates; dashed lines denote densities in the absence of particles. Grey lines mark the density of charged particles. Simulations were performed for quiet twilight conditions (Figure 1a).

**Figure 8.** As Figure 7, but for perturbed daytime conditions (Figure 1c).

**Figure 9.** Size spectra for proton hydrates at 86 km for various temperatures. Ionization conditions are as in Figure 1b (quiet daytime), neutrals are as in Figure 4. Black lines denote spectra in the absence of particles, gray lines denote spectra in the presence of 1000 cm$^{-3}$ particles of radius 10 nm.
Figure 10. Proton hydrate recombination coefficients as a function of cluster size. The laboratory measurements for \( n \leq 6 \) have been scaled to 130 K. The Natanson approach used in this paper is compared to the parameterization of Sugiyama [1994]. For comparison, recombination coefficients for \( \text{O}_2^+ \) and \( \text{NO}^+ \) are marked.

Figure 11. Ionic nucleation as a function of temperature, ionization and water abundance. The isolines represent nucleation rates of 0.03 cm\(^3\) s\(^{-1}\) (= 100 cm\(^3\) h\(^{-1}\)). The atmospheric density is 2\( \times \)10\(^{14}\) cm\(^{-3}\), corresponding to an altitude of about 86 km.

Figure 12. Dependence of heavy proton hydrates on atomic oxygen. Solid lines correspond to the O profile in Figure 5, dashed lines to a 10\( \times \) reduced O density. Simulations have been performed for quiet daytime conditions (Figure 1b) and perturbed daytime conditions (Figure 1c).