PROGRAM ABSTRACTS

Formation and Growth of Atmospheric Aerosols

September 8-9, 2006

Co-Chaired by Peter McMurry and Markku Kulmala

Preface: Workshop on the Formation and Growth of Atmospheric Aerosols *Peter H. McMurry and Markku Kulmala*
Modeling
Ken Carslaw
What can we learn from correlation studies of sulfuric acid and fine particle concentration profiles? *Kari E. Lehtinen, Ilona Riipinen, Sanna-Liisa Sihto, Ari Laaksonen and Markku Kulmala*
Gas-Phase Nucleation via Chemical Reactions *Steven L. Girshick*
Computational Chemistry
Dynamical Nucleation Theory: A Molecular-Level Approach to New Particle Formation *Bruce C. Garrett, Shawn M. Kathmann and Gregory K. Schenter*
Recent Quantum Chemical Results on Atmospheric Nucleation Processes *Theo Kurtén, Leena Torpo, Boris Bonn, Hanna Vehkamäki and Markku Kulmala*
Simulating Vapor—Liquid Nucleation of Water, Alkanes, Alkanols and Their Mixtures *J. Ilja Siepmann, Bin Chen, Ricky B. Nellas and Matthew E. Mckenzie*
Ion-Induced Nucleation
Atmospheric Ion Induced Nucleation *Edward R. Lovejoy, Karl D. Froyd, Joachim Curtius and Jan Kazil*
Ion-Mediated Nucleation as a Source of Atmospheric Particles *Fangqun Yu*
Contribution of Ion-Induced Nucleation on Tropospheric Nucleation *Lauri Laakso, Anne Hirsikko, Stéphanié Gagné, Miikka Dal Maso and Markku Kulmala*
Experimental Study of Heterogeneous Nucleation on Charged and Uncharged Nanoclusters *Paul M. Winkler, Gerhard W. Steiner, Georg P. Reischl, Aron Vrtala, Paul E. Wagner, Anca Hienola, Hanna Vehkamäki and Markku Kulmala*
Nucleation Experiments and Theory
Ari Laaksonen, Santtu Mikkonen, Antti-Pekka Hyvärinen, Kari Lehtinen, Sanna-Liisa Sihto and Markku Kulmala
Homogeneous Nucleation Rate Measurements and the Properties of Small Water Clusters *Barbara E. Wyslouzil, Yoojeong Kim, Gerald Wilemski, Judith Wölk and Reinhard Strey*
Ternary Nucleation Mechanisms and New Particle Formation *Robert McGraw*

Nuclear Molecular Clusters

Atmospheric Nucleation Rates from Laboratory Measurements of Molecular Clusters
Dave R. Hanson and E.R. Lovejoy

Towards Observations of Neutral Atmospheric Clusters: Results from Hyytiälä, Southern Finland
Ilona Riipinen, Markku Kulmala, Hanna Mannimen, Mikko Sipilä, Tuukka Petäjä, Genrik Mordas, Aadu Mirme, Marko Vana, Tuomo Nieminen, Lauri Laakso and Veli-Matti Kerminen

Do we know anything about the composition of coastal nanoparticles?
Gordon McFiggins, James Allan, Rachel Burgess, Hugh Coe, Michael Cubison, Russell Saunders, John Plane, Alfonso Saiz-Lopez, Carl Palmer, Lucy Carpenter and Frithof Küpper

Ions and Ion-Induced Nucleation

Precise Mobility Measurements and their Relevance in Atmospheric Nucleation Studies
Juan Fernández de la Mora

About the Studies of New Particle Formation and Growth Using Air Ion Spectrometers
M. Vana, E. Tamm, U. Hõrrak, A. Mirme, H. Tammet, A. Hirsikko, L. Laakso and M. Kulmala

Biogenic Aerosol Formation in a Native Australian Eucalypt Forest
Tanj Suni, Eva van Gorsel, Helen Cleugh, Ray Leuning, Steve Zegelin, Dale Hughes, Mark Kitchen, Richard Hurley, Larisa Sogacheva, Lauri Laakso, Anne Hirsikko, Miikka dal Maso, Timo Vesala and Markku Kulmala

Experimental Systems for Investigations of Ion-Induced Nucleation
M. Adachi and N. Yokoyama

Nucleation Involving Organics and H_2SO_4

Contributions of Organic Acids to New Particle Formation
Renyi Zhang

Measurements of Potential Aerosol Precursor Gases in the Rural and Coastal Atmosphere
H. Berresheim and C. Plass-Duelmer

The Growth Rate of Fresh Atmospheric Particles: Implications on Vapour Species and Nucleation Rate Estimates
Miikka Dal Maso, Tuukka Petäjä, Ilona Riipinen, Anne Hirsikko, Sanna-Liisa Sihto, Michael Boy, Laura Korhonen and Markku Kulmala

Composition of Freshly Nucleated Particles

Recent Progress in Quantifying the Chemical Composition of Nanoparticles Formed by Nucleation
James N. Smith, Fred L. Eisele and Peter H. McMurry

The Boreal Forest Aerosol Maintained by Terpene Emisions
Peter Tunved, Hans-Christen Hansson, Veli-Matti Kerminen, Markku Kulmala, Johan Ström, Keikki Lihavainen, Yrjö Viisanen, Miikka Dal Maso and Paasi Aalto

Jose Jimenez

POSTER ABSTRACTS

Formation and Growth of Atmospheric Aerosols

September 8-9, 2006

Co-Chaired by Peter McMurry and Markku Kulmala

	Poster Number
Atmospheric Observations	
Obtaining the Diameter Growth Rate and Particle Current During Nucleation and Growth Period from Measurements of Charge Distributions and Aerosol Size Distributions *Kenjiro Iida, Mark R. Stolzenburg and Peter H. McMurry*	P-A-1
Observations of Ultrafine Particles in Combination with Different Boundary Layer Processes *Birgit Wehner, Holger Siebert, Alfred Wiedensohler and Frank Stratmann*	P-A-2
Nucleation Events at a High Alpine Site: Particle Growth and Nucleation Rates *Bart Verheggen, Ernest Weingartner, Julie Cozic, Marko Vana, Pasi Aalto, Anne Hirsikko, Markku Kulmala and Urs Baltensperger*	P-A-3
Measurements and Modeling of Atmospheric Homogeneous Nucleation *Alicia K. Pettibone, William Eichinger, Spyros N. Pandis and Charles O. Stanier*	P-A-4
New Particle Formation in the Upper Troposphere and Lower Stratosphere: Recent Results from the HIAPER Progressive Science Missions *Shan-Hu Lee, David R. Benson, Li-Hao Young, James C. Wilson, William Montanaro, Jorgen Jensen, Jeff Stith, Christopher A. Davis, Teresa L. Campos, David Rogers and William A. Cooper*	P-A-5
Growth Rates of Freshly Nucleated Atmospheric Particles in Atlanta *Mark R. Stolzenburg, Peter H. McMurry, Hiromu Sakurai, James N. Smith, R. Lee Mauldin III, Fred L. Eisele and Charles F. Clement*	P-A-6
Laboratory Studies	
Aerosol Formation from Isoprene: Determination of Particle Nucleation and Growth Rates from Measured Size Distributions *Bart Verheggen, Jonathan Duplissy, Axel Metzger, Joseph Dommen, Ernest Weingartner, Andre Prevot and Urs Baltensperger*	P-L-1
Indoor Air Nucleation in the Presence of D-limonene *Eija Vartiainen, Markku Kulmala, Kaarle Hämeri, Taina Ruuskanen, Risto Taipale and Hanna Vehkamäki*	P-L-2
Effect of NH_3 on Nano-Particle Formation from SO_2 in Humid Air *Kenkichi Nagato and Tohru Kawabuchi*	P-L-3
Growth Rate Analysis of Gas-to-Particle Conversion in Smog Chamber Experiments *Michael Mozurkewich, Kristina Zeromskiene and Bart Verheggen*	P-L-4

Chemical Mechanisms	
Possible Gas Phase Approach to Understanding Tropospheric Nucleation *F.L. Eisele*	P-C-1
Effect of Formic Acid, Acetic Acid and Ammonia on Stability of Sulfuric Acid-Water Complexes *A.B. Nadykto and F. Yu*	P-C-2
The Role of Competitive Dynamic Condensation and Evaporation of NH_3, HNO_3, and HCl in the Growth of Freshly Nucleated Sulfuric Acid Particles *Rahul A. Zaveri and Richard C. Easter*	P-C-3
Cluster Non-Accommodation: Barriers to Small Cluster Growth and Their Effect on Atmospheric Particle Size Distributions *Chongai Kuang, Peter H. McMurry, Alon V. McCormick and Michael R. Zachariah*	P-C-4
Statistical Mechanics of Aqueous Sulfuric Acid and Ionic Clusters *Shawn M. Kathmann, Gregory K. Schenter and Bruce C. Garrett*	P-C-5
Modeling	
MALTE – Model to Predict New Aerosol Formation in the Lower Troposphere *Michael Boy, Olaf. Hellmuth, Hannele Korhonen, Douglas Nilsson, Douglas ReVelle, Andrew Turnipseed, Frank Arnold and Markku Kulmala*	P-M-1
Sensitivity of Modeled Number Concentrations to the Representation of New Particle Formation and Particle Emissions in Chemical Transport Models *Lim-Seok Chang, Douglas L. Wright, Ernie R. Lewis, Stephen E. Schwartz and Robert McGraw*	P-M-2
Evaluation of Homogeneous Nucleation Parameterizations used in 3-D Air Quality Models *Yang Zhang*	P-M-3
Instrumentation	
A New Nano-SMPS System for Measuring Size Distribution of Atmospheric Aerosols Below 3 nm *Kenjiro Iida, Mark R. Stolzenburg and Peter H. McMurry*	P-I-1
Measuring Aerosol Particles Below 3 nm by Condensation Particle Counter UF-02proto *Mikko Sipilä, Tuukka Petäjä, Hanna Manninen, Genrik Mordas, Ilona Riipinen and Markku Kulmala*	P-I-2
Direct Measurement of Neutral Molecular Clusters by Chemical Ionization Mass Spectrometry: Elucidating the Mechanisms of New Particle Formation in the Atmosphere *Mari E. Titcombe, Jeffrey T. Roberts, Peter H. McMurry, Lee Mauldin and Fred R. Eisele*	P-I-3
Aerosol Mass Spectrometry of New Particle Growth *Douglas R. Worsnop*	P-I-4

Preface: Workshop on the Formation and Growth of Atmospheric Aerosols

Peter H. McMurry[1], **Markku Kulmala**[2]
[1]*Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA*
[2]*Department of Physical Sciences, University of Helsinki, Helsinki, FIN-00014, Finland*

Recent observations have shown that new particle formation (NPF) occurs frequently in many regions of the atmosphere (Kulmala et al., 2004). NPF has been observed in polluted urban areas, above boreal forests, downwind of exposed tidal zones, in plumes from combustion sources, and in cloud outflows. Both biogenic and anthropogenic precursors apparently play a role this process. Particles formed by nucleation can increase total particle concentrations by several hundred percent, thereby affecting size distributions. NPF can also increase the concentrations of cloud condensation nuclei (CCN) (Ghan et al., 2001; Kerminen et al., 2005; Laaksonen et al., 2005). Therefore, NPF can have both direct and indirect radiative effects, and there is a need to account for this process in global climate models.

Evidence suggests that the chemical processes responsible for nucleation are different from those responsible for subsequent particle growth (Kulmala et al., 2000; Stolzenburg et al., 2005; Kulmala et al., 2006). There is strong evidence that sulfuric acid vapor often participates in particle formation, but the condensation of sulfuric acid and its associated water and ammonia may account for only a small fraction of the observed growth (Stolzenburg et al., 2005). It is essential to have models both for particle formation rates (nucleation) and growth. Nucleation rates determine the number of particles formed, while growth rates determine the time required for them to grow to CCN sizes as well as the probability that this will occur before they are scavenged by preexisting particles (Weber et al., 1997; Kerminen and Kulmala 2002; McMurry et al., 2005). The chemical processes responsible for nucleation and growth likely differ with time and location, and these differences need to be understood.

The most important climatic impact of new particle formation is probably on cloud formation and the associated radiative effects. It is essential that more work be done to quantify the impact of new particle formation on CCN concentrations and cloud properties.

This is the second international workshop on the formation and growth of atmospheric aerosols. The first was held at Hyytiälä, Finland (August 15-17, 2005). The purpose of the workshop is to bring together atmospheric scientists and others who have diverse perspectives on approaches that might be used to resolve the issues summarized above. Our goal is to develop models that are adequate for use in global climate models.

REFERENCES

Ghan, S. J., R. C. Easter, E. Chapman, H. Abdul-Razzak, Y. Zhang, R. Leung, N. Laulainen, R. Saylor and R. Zaveri (2001). "A physically-based estimate of radiative forcing by anthropogenic sulfate aerosol." J. Geophys. Res. **106**(5279-5294).

Kerminen, V. M. and M. Kulmala (2002). "Analytical formulae connecting the "real" and the "apparent" nucleation rate and the nuclei number concentration for atmospheric nucleation events." Journal of Aerosol Science **33**(4): 609-622.

Kerminen, V. M., H. Lihavainen, M. Komppula, Y. Viisanen and M. Kulmala (2005). "Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation - art. no. L14803." Geophysical Research Letters **32**(14): 14803.

Kulmala, M., K. E. J. Lehtinen and A. Laaksonen (2006). "Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulphuric acid concentration." Atmospheric Chemistry and Physics **6**: 787-793.

Kulmala, M., U. Pirjola and J. M. Mäkelä (2000). "Stable sulphate clusters as a source of new atmospheric particles." Nature **404**(6773): 66-69.

Kulmala, M., H. Vehkamaki, T. Petajda, M. Dal Maso, A. Lauri, V. M. Kerminen, W. Birmili and P. H. McMurry (2004). "Formation and growth rates of ultrafine atmospheric particles: a review of observations." J. of Aerosol Sci. **35**(2): 143-176.

Laaksonen, A., A. Hamed, J. Joutsensaari, L. Hiltunen, F. Cavalli, W. Junkermann, A. Asmi, S. Fuzzi and M. C. Facchini (2005). "Cloud condensation nucleus production from nucleation events at a highly polluted region - art. no. L06812." Geophysical Research Letters **32**(6): 6812.

McMurry, P. H., M. A. Fink, H. Sakurai, M. R. Stolzenburg, L. Mauldin, K. Moore, J. N. Smith, F. L. Eisele, S. Sjostedt, D. Tanner, L. G. Huey, J. B. Nowak, E. Edgerton and D. Voisin (2005). "A Criterion for New Particle Formation in the Sulfur-Rich Atlanta Atmosphere." Journal of Geophysical Research - Atmospheres **110**: D22S02.

Stolzenburg, M. R., P. H. McMurry, H. Sakurai, J. N. Smith, R. L. Mauldin, F. L. Eisele and C. F. Clement

(2005). "Growth rates of freshly nucleated atmospheric particles in Atlanta - art. no. D22S05." Journal of Geophysical Research-Atmospheres **110**(D22): S2205.

Weber, R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, D. J. Tanner and A. Jefferson (1997). "Measurements of new particle formation and ultrafine particle growth rates at a clean continental site." Journal of Geophysical Research - Atmospheres **102**(D4): 4375-4385.

What can we learn from correlation studies of sulfuric acid and fine particle concentration profiles?

Kari E. J. Lehtinen[1,3], **Ilona Riipinen**[2] , **Sanna-Liisa Sihto**[2] , **Ari Laaksonen**[3] **and Markku Kulmala**[2]
[1]*Finnish Meteorological Institute, Kuopio Unit, P.O.Box 1627, 70211, Kuopio, Finland*
[2]*Department of Physical Sciences , University of Helsinki, P.O.Box 64, 00014, Helsinki, Finland*
[1]*Department of Physics, University of Kuopio, P.O.Box 1627, 70211, Kuopio, Finland*

INTRODUCTION

Sulfuric acid is a key component in atmospheric aerosol formation. Several nucleation mechanisms, including binary, ternary and ion-induced nucleation, are likely to involve sulphuric acid. Some, if not the major, fraction of the particle growth can be explained by sulphuric acid condensation, especially in the smallest particle sizes. Sulphuric acid might also play a role in the so-called activation process, in which stable clusters containing sulphuric acid molecules will be activated for growth (Kulmala et al., 2005). It is therefore important to measure sulphuric acid concentrations and aerosol relevant parameters at the same time in order to quantify the contribution of sulphuric acid to both particle formation and growth.

The present study was inspired by the observation that on new particle formation days, the temporal evolution of the number concentration of nucleation mode particles seems to follow the concentration of sulphuric acid. In view of this, we reanalysed the data from the measurement campaign QUEST 2. The main goal of the QUEST-project (Quantification of Aerosol Nucleation in the European Boundary Layer) has been the qualitative and quantitative analysis of particle nucleation and growth in three European regions. During the QUEST 2 campaign in Hyytiala (17 March to 13 April 2003), sulphuric acid concentrations and particle number size distributions were measured continuously on 23 days. From these data various quantities, such as the formation and growth rate of aerosol particles, were calculated.

The general goal of this study is to get information about the aerosol formation processes below 3nm diameter, which is the lower limit of current instruments for measuring neutral atmospheric particles. More specifically, we aim to address the following questions: i) how sulphuric acid and nucleation mode particle concentrations are related to each other, ii) how large is the particle growth rate from 1 to 3nm and what is the reason for its variability, iii) which particle formation mechanism explains the measurement data best, and iv) how large are relevant activation/kinetic constants associated with the different particle formation mechanisms and how the values of these 15 constants vary as a function of measured parameters?

The investigation is based on a thorough correlation analysis of observed data as well as aerosol dynamics medelling studies using the UHMA model (Korhonen et al., 2003). The particle growth rate from 1 to 3nm will be estimated from the observed time shift between increasing sulphuric acid and ultrafine particles number concentration. Two different particle formation mechanisms will be tested, the recently-developed activation theory (Kulmala et al., 2005) and kinetic (barrierless) nucleation theory (McMurry and Friedlander, 1979).

METHODS

Particle number size distributions of atmospheric aerosol particles from 3 to 500nm were measured continuously, with 10-min time resolution, by a DMPS (Differential Mobility Particle Sizer) setup. The setup consists of two parallel differential mobility analyzers (DMAs) that classify particles in size ranges 3–10nm and 10–500 nm, the total number of size classes being 32. The sulphuric acid concentration was measured by a chemical ionization mass spectrometer (CIMS) built by the MPI-K Heidelberg (see Hanke et al., 2002). The sulphuric acid detection limit was 1×105 cm−3 and the relative measurement error 30%.

From the size distribution measurements, apparent formation rates at 3 nm J3 were estimated based on changes in the fine particle concentrations between 3 and 6 nm N36. These values were compared with the time evolution of the sulfuric acid concentration, aiming at finding simple power law type relationships. Then, by studying the power law exponents, one can obtain hints of the prevailing nucleation mechanism(s). The theories behind our correlation studies were tested using detailed aerosol dynamics modelling with the UHMA code. With known nucleation and iniitial growth mechanims and rates and an aerosol dynamics code one can generate useful test data for correlation studies and theoretical analyses.

RESULTS AND DISCUSSION

The concentration of 3–6nm particles was found to have approximately a power-law dependence on the sulphuric acid concentration, with an exponent value between 1 and 2. The results imply and activation type or kinetic nucleation mechanism, or a combination of the two mechanims.

Using time shift analysis based on this correlation, the growth rate from 1nm to 3nm has been determined. The mean value was 1.2 nm/h and a large fraction of it, on average about 50%, can be explained by the condensation of sulphuric acid.

From fittings to particle measurement data empirical nucleation coefficients were determined. The mean values of the activation and kinetic coefficients were 1.7×10^{-6} s^{-1} and 0.6×10^{-12} cm^3s^{-1}, respectively, being of the same order of magnitude as chemical reaction rate coefficients in the gas phase with vapour concentrations around 10^6–10^8 cm^{-3}.

The main conclusion from the UHMA studies is that drawing conclusions from exponents resulting from correlation studies of experimental data alone may be misleading and needs to be done with care. The same nucleation mechanism, but at different conditions (vapor and background aerosol profiles) may lead to surprisingly different power law exponents, when a correlation between sulfuric acid and fine particle concentrations is investigated.

Keywords: *Sulfuric acid, barrierless nucleation, activation, aerosol dynamics*

REFERENCES

Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A. (2005): Why formation rate of 3nm particles depends linearly on sulphuric acid concentration, *Atmos. Chem. Phys. Discuss*., 5, 11277–11293, 2005b.

Korhonen, H., Lehtinen, K. E. J., and Kulmala, M. (2004): Multicomponent aerosol dynamics model UHMA: model development and validation, *Atmos. Chem. Phys*., 4, 757–771.

McMurry, P. H. and Friedlander, S. K. (1979): New particle formation in the presence of an aerosol, *Atmos. Environ*., 13, 1635–1651.

Hanke, M., Uecker, J., Reiner, T., and Arnold, F. (2002): Atmospheric peroxy radicals: ROXMAS, a new mass-spectrometric methodology for speciated measurements of HO2 and Sigma RO2 and first results, *Int. J. Mass Spectr*., 213(2–3), 91–99.

Gas-Phase Nucleation via Chemical Reactions

Steven L. Girshick
Department of Mechanical Engineering , University of Minnesota, Minneapolis, MN 55455, USA

Usual nucleation theory treats the situation where one or more supersaturated vapors condense to grow stable nuclei of a new phase, where the condensation is implicitly a physisorption process, *i.e.* does not involve making or breaking chemical bonds.

However under many conditions nucleation in the gas phase occurs even without the presence of any one specific supersaturated vapor, and the growing cluster may have a different chemical composition than any of the vapor phase species that contribute to its growth. An obvious example is carbon soot formation in flames, which under most conditions is not driven by condensation of monatomic carbon vapor. Rather the driving force for nucleation is the departure of the overall system from chemical equilibrium, *i.e.* the departure of the system from the minimum in its Gibbs free energy at given pressure and temperature. In this case the path to nucleation is that C_nH_m molecules grow by chemical reactions with other hydrocarbons, adding carbon atoms while often eliminating hydrogen back to the gas phase, and can shrink by oxidation.

Usual nucleation theory is obviously inadequate to treat this situation, yet such "chemical nucleation" scenarios are arguably commonplace. Any system in which a film is grown on a macroscopic substrate by chemical vapor deposition can be considered a candidate for chemical nucleation of particles in the gas phase. For example, silane, activated either thermally or by a plasma, is used to grow silicon thin films, and is also known to be prone to gas-phase nucleation. Under most conditions it can be shown that particle formation from silane is unlikely to be caused by condensation of monatomic silicon vapor. Rather it occurs via sequential growth reactions involving various silicon hydride molecules and radicals (and, in the plasma case, ions).

We have developed detailed chemical kinetic models for nucleation in silane, driven both thermally (Swihart and Girshick, 1999) and by plasma (Bhandarkar *et al.*, 2000). These models involve large coupled sets of chemical rate equations, including species containing up to some arbitrary number (*e.g.* 10) of silicon atoms. They require rational schemes for the estimation of reaction rate parameters and thermodynamic properties for large molecules and radicals, as in general these are known only for the smallest molecules. Reaction rate parameters for larger molecules and radicals are estimated by grouping silicon hydrides and their reactions into a few classes, and then using appropriate scaling laws.

Thermodynamic properties (enthalpy and entropy) are needed so that, given a forward rate constant for a reaction, the reverse rate constant can be determined. We use group additivity to build on what is known about small molecules and radicals so as to estimate thermodynamic properties for larger species. In this approach, enthalpies and entropies are assigned to specific bonding configurations ("groups"). The total enthalpy or entropy for a molecule is estimated by summing the group addivity values for all the groups of which that molecule is composed. Group additivity has proven to be a powerful approach for estimating the properties of hydrocarbons (O'Neal and Benson, 1969) and partially halogenated hydrocarbons (Benson, 1976), and it is well suited to the silicon hydride system. We are currently developing a group additivity scheme for fluorocarbons (VanOtterloo *et al.*, 2005).

As regards nucleation theory, the salient point is that chemical nucleation involves growing clusters by making and breaking chemical bonds, and any realistic model must account for corresponding free energy changes. In the future *ab initio* computational chemistry will become sufficiently powerful to calculate properties and reactivities for clusters of large sizes for many chemical species. However for most systems of interest in chemical nucleation this is not yet practical, and methods such as group addivity provide a powerful tool for making realistic estimates.

In many cases of chemical nucleation one does not know *a priori* what are the dominant pathways to nucleation, and it is therefore necessary to solve a large set of coupled rate equations. The size of this set can usually be substantially reduced using methods of chemical mechanism reduction. But in some cases it is likely that nucleation can be described by a simple sequence of reversible reactions. In that case, we have shown that the mathematical formalism of classical nucleation theory can be used to derive a simple expression for the nucleation rate (Girshick, 1997), analagous to the "summation" form of the classical expression for the rate of homogeneous nucleation.

In the context of atmospheric aerosols, soot formation in flames is of obvious importance, but otherwise it is not clear whether chemical nucleation is an important mechanism in the atmosphere. Nevertheless, it is clear that classical approaches to nucleation (*i.e.* approaches that make the approximation that properties such as surface tension of small clusters are identical to that of the bulk condensed phase) are inadequate to provide a quantitive description of nucleation for even the simplest scenarios. Given this predicament, it should be noted that even "physically" driven nucleation (involving cluster growth by physisorption rather than chemical reactions) can be viewed as simply a special case of chemical nucleation. It is thus the case that "usual" condensation/evaporation-based self-nucleation, binary nucleation and ion-induced nucleation can all be viewed within the framework of chemical kinetics theory. As more accurate data on the properties of small clusters become available, one can therefore anticipate that these various types of nucleation will all be treated within a common framework, that utilizes an entirely atomistic approach to modeling nucleation in terms of a set of chemical reactions, where all species and reactions are assigned their own unique properties and rate parameters.

Keywords: *Chemical nucleation, group additivity*

REFERENCES

Benson, S. W. (1976) *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd edition (Wiley, New York).

Bhandarkar, U., Swihart, M. T., Girshick, S. L. and Kortshagen, U. (2000) Modeling of silicon hydride clustering in a low-pressure silane plasma, *J. Phys D,* 33, 2731-2746.

Girshick, S. L. (1997) Theory of nucleation from the gas phase by a sequence of reversible chemical reactions, *J. Chem. Phys.,* 107, 1948-1952.

O'Neal, H. E. and Benson, S. W. (1969) Entropies and heat capacities of free radicals, *Int. J. Chem. Kinet.,* 1, 221.

Swihart, M. T. and Girshick, S. L. (1999) Thermochemistry and kinetics of silicon hydride cluster formation during thermal decomposition of silane, *J. Phys. Chem. B*, 103, 64-76.

VanOtterloo, M., Girshick, S. L. and Roberts, J. T. (2005) Thermodynamic properties of fluorocarbons, 17th International Symposium on Plasma Chemistry, Toronto, Aug. 7-12, 2005, *Abstracts and Full-Papers CD*, pp. 219-220, full paper on compact disk.

Dynamical Nucleation Theory: A Molecular-Level Approach to New Particle Formation

Bruce C. Garrett, Shawn M. Kathmann, and Gregory K. Schenter
Chemical Sciences Division, Pacific Northwest National Laboratory

Vapor-phase nucleation is a dynamical rare event process in which the macroscopic process of new particle formation is controlled by the dynamics of nanoscale clusters. The goal of molecular theories of nucleation is to obtain nucleation rates starting from the molecular interaction potential. A reliable molecular-level treatment of nucleation requires (*i*) accurate descriptions of the interaction potentials, (*ii*) a consistent theoretical approach that connects the interaction potential to the nucleation rate, and (*iii*) adequate simulation procedures to evaluate quantities of interest. This presentation will focus on the development of Dynamical Nucleation Theory (DNT),[1-3] which addresses issue (*ii*), and what this new theoretical framework has taught us about new particle formation. We will discuss issues (*i*) and (*iii*) as they relate to the requirements of computational chemistry and molecular simulation methods for use within this framework. We restrict our discussion to nucleation in aqueous systems.

For nucleation in a single component system (e.g., pure water), the starting point is the assumption that addition and removal of monomers from clusters adequately describes the nucleation kinetics,

$$N_1 + N_{i-1} \underset{\alpha_i}{\overset{\beta_{i-1}}{\rightleftarrows}} N_i, \; i=1,2,\ldots$$

where N_1 is the number of monomers, N_i (i>1) is the number of clusters containing i monomers, and α_i and β_i are evaporation and condensation rate constants, respectively. The nucleation rate is obtained by solving the kinetic equations. DNT was the first molecular theory to directly calculate the evaporation and condensation rate constants using a consistent molecular theory. (Note that DNT can be extended to treat multi-component systems,[3] such as those important in the atmosphere, and to go beyond the limitation of including only monomer evaporation and condensation.) We view the processes of evaporation and condensation as gas-phase dissociation and association reactions. This view of nucleation kinetics is quite different than the perspective generally encountered in the nucleation literature, which describes nucleation as density fluctuations in a supersaturated fluid. Given the large average distance between monomers and clusters in the vapor ($>10^4$-10^5 Å for water at a supersaturation of 5), the view of nucleation as a gas-phase reaction mechanism is quite reasonable. Variational transition state theory (VTST)[4] provides a consistent and accurate approach to calculate the required reaction rate constants.

VTST approximates rate constants by calculating the equilibrium one-way flux through a dividing surface separating reactants from products. By making the fundamental assumption of transition state theory, an inherently dynamical process can be characterized in terms of equilibrium statistical mechanical averages, e.g., partition functions that are computed from knowledge of the interaction potential. A crucial issue in transition state theory is the definition of the dividing surface. In a classical world, the fundamental assumption of transition state theory causes the VTST rate constant to be overestimated, and the best estimate of the rate constant can be obtained by variationally optimizing the dividing surface. The dividing surface that minimizes the reactive flux provides a practical means of identifying the most relevant configurations associated with the rare event process.

Clusters important in nucleation are inherently unstable. For small clusters the evaporation rate is higher than the condensation rate. As the cluster size grows the condensation rate increases, while the evaporation rate usually decreases. The critical nucleus is defined as the cluster size for which the evaporation and condensation rates are approximately equal. Clusters larger than the critical nucleus have condensation rates higher than evaporation, and they spontaneously grow into the macroscopic phase. The low stability of precritical clusters requires the development and application of appropriate molecular simulations that correctly account for the *anharmonicity* of these systems. There are two different types of anharmonicity that are important in these systems: global anharmonicity resulting from a large number of local minima in these highly fluctuating molecular clusters, and local anharmonicity of the vibrations for a given cluster configuration. The need to use statistical mechanical approaches that sample the relevant configuration space of these highly anharmonic clusters limits the types of interaction potentials that can be used. For small clusters with only a few molecules, it is feasible to use electronic structure methods, calculated ‘on-the-fly’ in molecular simulations. However, for most of our studies we are interested in more qualitative information about the nucleation process, and for those types of studies, it is adequate to use analytical functional forms for the interaction potential, which are generally fitted to electronic structure as well as empirical data.

Our studies have provided understanding of the extreme sensitivity of nucleation rates,[2] which has important implications for the role of trace species in the atmosphere on nucleation of new particles.[3] By applying sensitivity analysis to the kinetic mechanism of nucleation, we showed that the nucleation rate is most sensitive to all precritical cluster rate constants when the evaporation and condensation rate constants are treated as independent variables. In contrast, the nucleation rate is most sensitive to those clusters near the critical cluster when the evaporation rate constant and equilibrium cluster populations are treated as the independent variables. We also analyzed the sensitivity of the kinetic parameters and the nucleation rate on the underlying interaction potential. We have demonstrated that the sensitivity of nucleation rates to the interaction potential is determined primarily by changes in the equilibrium clusters populations, which in turn are determined from the cluster Helmholtz free energies. It was shown that systematic shifts in the Helmholtz free energies by 0.5 kcal/mol for each cluster lead to changes in the nucleation rate by over 10 orders of magnitude. Favorable interactions between water molecules and trace components will ultimately lower the absolute free energy. This absolute free energy, in turn, will affect the distribution function of the critical cluster. Studies of these effects require a molecular approach, such as DNT, in which the influence of the trace species is explicitly included via interaction potentials for that species.

[1] G. K. Schenter, S. M. Kathmann, and B. C. Garrett, *Phys. Rev. Lett.*, **82**, 3484 (1999). Dynamical Nucleation Theory: A New Molecular Approach to Vapor-Liquid Nucleation; G. K. Schenter, S. M. Kathmann, and B. C. Garrett, *J. Chem. Phys.*, **110**, 7951 (1999). Variational Transition State Theory of Vapor Phase Nucleation; S. M. Kathmann, G. K. Schenter, and B. C. Garrett, *J. Chem. Phys.*, **111**, 4688 (1999). Dynamical Nucleation Theory: Calculation of Condensation Rate Constants for Small Water Clusters; G. K. Schenter, S. M. Kathmann, and B. C. Garrett, *J. Chem. Phys.*, **116**, 4275 (2002). Dynamical Benchmarks of the Nucleation Kinetics of Water

[2] S. M. Kathmann, G. K. Schenter, and B. C. Garrett, *J. Chem. Phys.*, **116**, 5046 (2002). Understanding the Sensitivity of Nucleation Kinetics: A Case Study on Water

[3] S. M. Kathmann, G. K. Schenter, and B. C. Garrett, *J. Chem. Phys.*, **120**, 9133 (2004). Multicomponent Dynamical Nucleation Theory and Sensitivity Analysis

[4] D. G. Truhlar, B. C. Garrett, and S. J. Klippenstein, *J. Phys. Chem.*, **100**, 12771 (1996). The Current Status of Transition State Theory

Recent Quantum Chemical Results on Atmospheric Nucleation Processes

Theo Kurtén[1], Leena Torpo[1], Boris Bonn[1], Hanna Vehkamäki[1] and Markku Kulmala[1]
[1]*Department of Physics, University of Helsinki, P.O. Box 64, 00014 Helsingin Yliopisto, Finland*

INTRODUCTION

In atmospheric conditions, new-particle formation has been thought to involve sulfuric acid and water molecules, with possible contributions from ammonia and some (yet unknown) organic species. Attempts have been made to model particle formation using quantum chemical methods (Bandy and Ianni, 1998; Ianni and Bandy, 1999; Re *et al.* 1999) but previous studies have failed in two important respects. First, the calculated binding energies for the sulfuric acid – water clusters are too low, leading to predicted hydrate concentrations orders of magnitude lower than the experimental observations. Second, the experimentally observed strong nucleation-enhancing effect of ammonia (Hanson and Eisele, 2002) has not been predicted by the quantum chemical studies. Thus, the three central questions in current quantum chemical nucleation studies are the following:

1. Explain the discrepancies between predicted and observed degrees of hydration for sulfuric acid.
2. Explain why earlier computations fail to predict the formation of ammonia-containing clusters.
3. Determine the identities of the organic species participating in nucleation.

Using our recent computational results, we have been able to answer question 1 and question 2 partially. We have also proposed a plausible candidate for the organic species participating in nucleation, the stabilized Criegee intermediate-, with supporting preliminary computational information.

COMPUTATIONAL DETAILS

Our computations have been performed using the Dmol3 (MSI, 2001; used for the PW91/DNP calculations) and Gaussian 03 (Frisch *et al.*, 2004; used for all other calculations) program suites.

HYDRATION OF H_2SO_4

In our recent error analysis (Kurtén *et al.* 2006), we have assessed the contribution of different error sources to the observed discrepancies between experimental and predicted degrees of hydration for sulfuric acid. We have demonstrated that for density functional (DFT) calculations employing moderately large basis sets with diffuse and multiple polarization functions, basis set effects and the neglect of vibrational anharmonicity cause only small (<0.5 kcal/mol) errors in the calculated free energies of hydration. Thus, *e.g.* the difference of about 1-3 kcal/mol between the calculated and measured (Hanson and Eisele, 2000) free energy of hydration of sulfuric acid is primarily caused by the unsatisfactory description of hydrogen bonds by the B3LYP functional used in most previous studies. It should be noted that the corrected results of al Natsheh *et al.* (2004, erratum published 2006), who used the PW91 functional with a moderately large basis set, confirm the same conclusion. Unfortunately, extremely demanding (coupled-cluster with infinite basis set extrapolations) calculations are required to reliably replicate the experimental results.

Our error analysis demonstrates that future calculations on similar systems should be carried out using methods other than B3LYP. However, there is no single optimal choice for this. PW91 replicates the few available experimental results relatively well, and has the advantage of being quite well-known, but has performed quite badly in most recent benchmarking studies. The newer generation of hybrid-meta-GGA functionals (such as MPW1B95, B97-2 or M05-2X) perform better, but are heavily parametrized and often unavailable in commercial software packages. MP2 perturbation theory, unlike all current density functionals, is capable of describing dispersion interactions (which play a non-negligible role in H-bonding), and should therefore be more systematically reliable, but is computationally much more demanding.

ROLE OF AMMONIA IN NUCLEATION

Previous quantum chemical studies investigating the role of ammonia in nucleation only studied clusters containing one sulfuric acid. Our recent computations on clusters containing 2-3 sulfuric acid molecules demonstrate that the binding of ammonia to the clusters is significantly increased by the addition of acid molecules. From an atmospheric perspective, the most relevant parameter is the difference in the reaction free energies for the addition of water and ammonia to the clusters. Due to error cancellation, this difference is less sensitive to the choice of computational method than the free energies themselves.

Our PW91/DNP calculations predict that at 265K, the reaction free energy difference increases from around 3.5-5.5 kcal/mol for one-acid clusters to up to 12 kcal/mol for some of the two-acid clusters. Due to the significantly (*ca.* 8 orders of magnitude) higher atmospheric concentration of water compared to ammonia, a difference of around 10 kcal/mol would be required for ammonia-containing clusters to be visible in the cluster distribution. This is observed for some size classes of two-acid clusters, but for most atmospherically reasonable conditions our simulated equilibrium cluster distributions are still dominated by ammonia-free clusters. However, our results indicate that further calculations *e.g.* on clusters containing more than one ammonia molecule or even more acid molecules might better demonstrate the nucleation-enhancing effect of ammonia.

THE CRIEGEE INTERMEDIATE AS A PRECURSOR FOR ORGANIC NUCLEATION

Criegee intermediates are biradicals formed via several steps in the ozonolysis of alkenes, *e.g* terpenes:

$$R_1R_2C=CR_3R_4 + O_3 \Rightarrow R_1R_2CO + R_3R_4COO^{\ddagger} \qquad (1)$$

Where $R_1 \ldots R_4$ are functional groups and ‡ denotes vibrational excitation. Small Criegee intermediates rapidly undergo unimolecular decomposition, but larger compounds are expected to be collisionally stabilized, and react with *e.g.* water, carbonyl compounds or organic acids. We have recently proposed a mechanism for the reaction of stabilized Criegee intermediates (sCI) with sulfuric acid:

$$R_3R_4COO + H_2SO_4 \Rightarrow R_3R_4C(OOH)OSO_3H \qquad (2)$$

where the product is a peroxide sulfate complex stabilized by a OOH...O=S hydrogen bond.

The reaction is found to be strongly exothermic for all studied species, ranging from one- and two carbon model species to the atmospherically relevant α-pinene – and β–caryophyllene – derived sCIs. Unfortunately, since sCIs are rather energetic (and hence react exothermically with almost anything), thermochemical calculations are not enough to assess the atmospheric importance of the postulated reaction. (This will probably apply to many potential organic nucleation pathways, not just this specific case.) Kinetic calculations, on the other hand, are much more difficult to perform accurately, and are made even more complicated by the large size and biradical nature of the atmospherically interesting sCIs.

Preliminary kinetics calculations on the CH_3COOCH_3 model species (at the B3LYP/aug-cc-pV(D+d)Z level, with single-point calculations at the CCSD/aug-cc-pV(D+d)Z level) indicate that the barrier for reaction (2) is very low (under 0.1 kcal/mol), while the corresponding reaction with water has a significant barrier of over 12 kcal/mol. If the same results are assumed to apply for larger sCIs, and the reaction with water is assumed to be the major sink reaction, application of elementary transition state theory and a steady-state approximation can be used to calculate an order-of-magnitude estimate for the production rate of peroxide complexes from reaction 2. Using reasonable ranges of values for reactant concentrations (Atkinson *et al.* 2005, Boy *et al.* 2005), we have estimated this production rate to be on the order of 10^3 to 10^6 molecules cm^{-3} s^{-1}. This is probably large enough to contribute significantly to observed organic nucleation events. However, the uncertainties (*e.g.* with respect to competing sink reactions) are considerable.

CONCLUSIONS

The differences between previous computational studies and experiments concerning the hydration energetics of sulfuric acid have been shown to be related to the B3LYP density functional, while discrepancies concerning the role of ammonia in nucleation are at least partly related to the lack of multiple-acid clusters in the studies. Preliminary thermochemical and kinetic computations indicate that a reaction between sulfuric acid and stabilized Criegee radicals may play a role in observed organic nucleation.

Keywords: *Quantum chemistry, sulfuric acid, ammonia, Criegee intermediate, organic nucleation*

REFERENCES

Al Natsheh *et al.* (2004): Sulfuric Acid and Sulfuric Acid Hydrates in the Gas Phase: A DFT Investigation. *J. Phys. Chem. A 108*, 8914-8929. Erratum in *J. Phys. Chem. A 110*, 7982-7984.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R. F., Hynes, R. G., Jenkin, M.E., Rossi, M.J. & Troe, J. (2005*) Atmos. Chem. Phys.*, 5, 6295-7168.

Boy, M. *et al.* (2005) *Atmos. Chem. Phys.* 5, 863-878.

Bandy, A. R., and Ianni, J. C. (1998). Study of Hydrates of H_2SO_4 Using Density Functional Theory, *J. Phys. Chem. A* 102, 6533-6539.

Frisch, M. J. *et al.* (2004). Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, U.S.A.

Hanson, D. R. and Eisele. F. L. (2000). Diffusion of H_2SO_4 in Humidified Nitrogen: Hydrated H_2SO_4. *J. Phys. Chem. A* 104, 1715.

Hanson, D. R. and Eisele, F. L. (2002) Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system. *J. Geophys. Res. D107*, 10.1021/2001JD001100

Ianni, J. C., and Bandy, A. R. (1999). A Density Functional Theory Study of the Hydrates of NH3*H2SO4 and Its Implications for the Formation of New Atmospheric Particles, *J. Phys. Chem. A* 103, 2801-2811.

Kurtén, T., Sundberg, M., Vehkamäki, H. and Kulmala, M. (2006). An *Ab Initio* and Density Functional Theory Reinvestigation of Gas-Phase Sulfuric Acid Monohydrate and Ammonium Hydrogensulfate. *J. Phys. Chem. A* 110, 7178-7188.

MSI, 2001: DMol3 version 4.21.

Re, S., Osamura, Y. and Morokuma, K. (1999). Coexistence of Neutral and Ion-Pair Clusters of Hydrated Sulfuric Acid H2SO4(H2O)n (n= 1-5) - A Molecular Orbital Study, *J. Phys. Chem. A* 103, 3535-3547.

Simulating Vapor—Liquid Nucleation of Water, Alkanes, Alkanols, and Their Mixtures

J. Ilja Siepmann[1], **Bin Chen**[2] , **Ricky, B. Nellas**[2], **and Matthew E. Mckenzie**[2]
[1]*Departments of Chemistry and of Chemical Engineering and Materials Science and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455-0431, U.S.A.*
[2]*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, U.S.A.*

INTRODUCTION

Nucleation, a fundamental first step in phase transitions, plays a critical role in many processes of environmental and technological importance. In particular, due to its relevance for atmospheric processes, the nucleation of water and of aqueous mixtures has been the focus for a great deal of experimental and theoretical investigations.

In this presentation, we discuss the use of advanced molecular simulation techniques and transferable force fields to predict nucleation free energy profiles and cluster abundances and to provide molecular-level information on the composition and structure of critical nuclei for water, alkanes, alcohols, and their mixtures.

SIMULATION METHODS

Since nucleation is a rare event that involves crossing a relatively high free energy barrier, special simulation approaches are required to sample the nucleation free energy barrier and to investigate the critical nucleus (i.e., the transition state). Over the past few years, we have developed a very efficient approach, called AVUS-HR, for the study of nucleation phenomena which combines the aggregation-volume-bias Monte Carlo (AVBMC) algorithm with self-adaptive umbrella sampling and histogram-reweighting techniques (Chen *et al.*, 2001, 2002, 2005). For molecular systems, the efficiency can be further improved through the use of configurational-bias Monte Carlo moves.

Alkanes and alcohols are modeled by the TraPPE (transferable potentials for phase equilibria) force field (http://www.chem.umn.edu/groups/siepmann/trappe.intro.php) and various force fields are used for water.

RESULTS AND DISCUSSION

AVUS-HR simulations for the nucleation of neat water over a temperature range from 200 to 300 K and the concentration of water clusters in the atmosphere at elevations up to 15 km show that (i) ice nucleation is not present for the thermodynamic conditions and cluster-size range investigated here, i.e., the critical nuclei possess liquid-like structures, and (ii) the atmospheric concentrations of water clusters under homogeneous conditions are very low (Chen *et al.*, 2005). Simulations of the nucleation for water/ethanol, water/*n*-nonane, ethanol/*n*-nonane, and water/*n*-nonane/1-butanol mixtures demonstrate that these non-ideal mixtures exhibit strikingly distinct nucleation free energy maps and, hence, follow different nucleation pathways that challenge current nucleation theories (Chen, et al., 2003; McKenzie and Chen, 2006). It is shown that these distinct nucleation free energy maps are consistent with the different non-ideal behaviors observed experimentally. Furthermore, structural analysis and snapshots of near-critical clusters provide insight on the nucleation pathways for these mixtures.

Keywords: *Vapor-liquid Nucleation, Nucleation Pathway, Binary and Ternary Mixtures, Non-idealities.*

REFERENCES

Chen, B., Siepmann, J. I., Oh, K. J., and Klein, M. L. (2001). Aggregation-volume-bias Monte Carlo simulations of vapor-liquid nucleation barriers for Lennard-Jonesium, *J. Chem. Phys*. 115, 10903-10913.

Chen, B., Siepmann, J. I., Oh, K. J., and Klein, M. L. (2002). Simulating vapor-liquid nucleation of *n*-alkanes, *J. Chem. Phys*. 116, 4317-4329.

Chen, B., Siepmann, J. I., and Klein, M. L. (2003). Simulating the nucleation of water/ethanol and water/*n*-nonane mixtures: Mutual enhancement and two-pathway mechanism, *J. Am. Chem. Soc*. 125, 3113-3118.

Chen, B., Siepmann, J. I. and Klein, M. L. (2005). Simulating vapor-liquid nucleation of water: A combined histogram-reweighting and aggregation-volume-bias Monte Carlo investigation for fixed-charge and polarizable models, *J. Phys. Chem. A*, 109, 1137-1145.

McKenzie, M. E., and Chen, B. (2006). Unravelling the peculiar nucleation mechanisms for non-ideal binary mixtures with atomistic simulations, *J. Phys. Chem. B*, 110, 3511-3516.

Financial support from the National Science Foundation (CTS-0138393, CTS-0553911, and CHE-0448918) is gratefully acknowledged.

Atmospheric Ion Induced Nucleation

Edward R. Lovejoy[1], **Karl D. Froyd**[1,2], **Joachim Curtius**[3], **and Jan Kazil**[1,2,4]
[1]*NOAA Earth System Research Laboratory, Boulder, Colorado, USA*
[2]*CIRES, University of Colorado, Boulder, Colorado, USA*
[3]*Institute for Atmospheric Physics, University of Mainz, Mainz, Germany.*
[4]*National Research Council Postdoctoral Fellow*

Ion induced nucleation (IIN) is potentially an important source of new atmospheric particles, and is of particular interest because it may be a mechanism to couple solar activity (which modulates atmospheric ionization) and cloud properties (that are affected by particle size distributions) (Carslaw et al., 2002). The quantitative understanding of ion induced nucleation rates depends critically on knowledge of the thermodynamics of the cluster ions involved in nucleation. Our work has focused on experimental studies of the thermodynamics of small positive and negative $H_2SO_4/NH_3/H_2O$ cluster ions (Froyd et al., 2003a, 2003b, Curtius et al., 2001, Lovejoy and Curtius 2001). This work has evolved into a kinetic nucleation model based on laboratory thermodynamics of small H_2SO_4/H_2O cluster ions (Lovejoy et al., 2004, Kazil and Lovejoy, 2004). Negative H_2SO_4/H_2O ions have a higher affinity for H_2SO_4 and are more likely to nucleate than the positive ions. Binary H_2SO_4/H_2O negative IIN is predicted to be an efficient nucleation mechanism throughout the free troposphere. The binary H_2SO_4/H_2O IIN model reproduces observations of ultrafine particles in the free troposphere and lower stratosphere, but does not consistently predict the observed boundary layer nucleation events (Lee et al. 2003, Lovejoy et al., 2004). At temperatures below about 220 K, the neutral binary mechanism can overwhelm the ion mechanism (D. Hanson, private communication). Recent measurements of atmospheric negative ions (Eisele et al, 2006) show that the $HSO_4^-(H_2SO_4)_x$ cluster ion distribution is consistent with the measured cluster ion thermodynamics, and that the kinetics of ion growth may be more complicated than currently assumed in IIN models. The role of ternary $H_2SO_4/NH_3/H_2O$ IIN is less well defined than the role of the binary system. The limited ternary positive ion thermodynamics suggest that for boundary layer conditions, NH_3 may actually inhibit nucleation, relative to the positive binary system. There is insufficient negative ternary ion thermodynamic data to draw any conclusions regarding the nucleation potential of this system. In this talk I will present an overview of IIN with an emphasis on what we know about the thermodynamics of the binary H_2SO_4/H_2O and the ternary $H_2SO_4/NH_3/H_2O$ systems. I will discuss the influence of the thermodynamics on the efficiency of IIN under atmospheric conditions, and compare with current knowledge for the corresponding neutral systems. I will conclude by commenting on the uncertainties in the thermodynamics and kinetics of ion-induced nucleation.

Keywords: *Nucleation, Ions, Ion clusters*

REFERENCES

Carslaw, K. S., R. G. Harrison, and J. Kirby, J. (2002), Cosmic Rays, Clouds, and Climate, *Science*, *298*, 1732-1737.

Curtius, J., K. D. Froyd, and E. R. Lovejoy (2001), Cluster ion thermal decomposition (I): Experimental kinetics study and ab initio calculations for $HSO_4^-(H_2SO_4)_x(HNO_3)_y$, *J. Phys. Chem. A*, *105*, 10867-10873.

Eisele, F. L., E. R. Lovejoy, E. Kosciuch, K. F. Moore, R. L. Mauldin III, J. N. Smith, P. H. McMurry, and K. Iida (2006), Negative atmospheric ions and their potential role in ion-induced nucleation, *J. Geophys.Res.*,*111*,D04305,doi:10.1029/2005JD006568.

Froyd, K. D., and E. R. Lovejoy (2003a), Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O. 1. Positive ions, J. Phys. Chem. A, 107, 9800-9811.

Froyd, K. D., and E. R. Lovejoy (2003b), Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O. 2. Measurements and ab initio structures of negative ions J. Phys. Chem. A, 107, 9812-9824.

Kazil, J. and E. R. Lovejoy (2004), Tropospheric ionization and aerosol production: A model study, J. Geophys.Res., 109, D19206, doi:10.1029/2004JD004852

Lee, S. H., J. M. Reeves, J. C. Wilson, D. E. Hunton, A. A. Viggiano, T. M. Miller, J. O. Ballenthin, and L. R. Lait (2003), Particle Formation by Ion Nucleation in the Upper Troposphere and Lower Stratosphere, *Science, 301*, 1886-1889.

Lovejoy, E. R., and J. Curtius (2001), Cluster ion Thermal decomposition (II): Master equation modeling in the low-pressure limit and fall-off regions. Bond energies for $HSO_4^-(H_2SO_4)_x(HNO_3)_y$, *J. Phys. Chem. A, 105, 10873.*

Lovejoy, E. R., J. Curtius, and K. D. Froyd (2004), Atmospheric ion-induced nucleation of sulfuric acid and water, *J. Geophys. Res. 109*, D08204, doi:10.1029/2003JD004460.

This work was supported in part by the NOAA Climate and Global Change Program.

Ion-Mediated Nucleation as a Source of Atmospheric Particles

Fangqun Yu
Atmospheric Sciences Research Center, State University of New York at Albany, 251 Fuller Road, Albany, 12203, New York, USA

INTRODUCTION

Nucleation frequently observed at various locations worldwide is an important source of atmospheric aerosols (Kulmala et al., 2004). Binary H_2SO_4-H_2O homo-geneous nucleation can't explain the observed nucleation events in the lower troposphere. Ternary homogeneous nucleation (THN) theory and ion-mediated nucleation have been proposed as alternative nucleation mechanisms. The actual role of NH_3 in the atmospheric nucleation remains unclear because the difference between experimental results and predictions of THN is excessively large (Yu, 2006a). Simulations based on a kinetic THN model constrained using the experimental data indicate that the contribution of THN to the particle formation is very limited (Yu, 2006a).

We have developed a second-generation ion-mediated nucleation (IMN) model (Yu, 2006b). The new model explicitly treats the evaporation of neutral and charged clusters and it describes the evolution of the size spectra and composition of both charged and neutral clusters/particles ranging from small clusters of few molecules to large particles of several micrometers in diameter. Results obtained using the second generation IMN model, in which the most recent thermodynamic data for neutral and charged H_2SO_4-H_2O clusters were used, suggest that ion-mediated nucleation of H_2SO_4-H_2O can lead to a significant production of new particles in the lower atmosphere (including the boundary layer) under favorable conditions. In this presentation, we discuss some of our recent studies and results based on the IMN model, focusing on IMN as a source of atmospheric aerosols.

SIMULATIONS AND RESULTS

In the atmosphere, the nucleation and growth processes are coupled. The freshly nucleated particles are typically ~ 2 nm or smaller in size; however it has been frequently observed that these particles can grow to the sizes of cloud condensation nuclei within a day. It has also been found that organics appear to dominate the growth of nucleated particles in many observed nucleation and growth events.

Figure 1 shows the evolution of the positively charged, negatively charged, and total clusters/ particles, with the dependence of $[H_2SO_4]$ and [organics] on local time (t, in hr) parameterized as $[H_2SO_4]=1.5\text{x}10^7\sin^2[\pi(t\text{-}4)/12]$, $[\text{organics}]=5\text{x}10^7 \sin^{0.5}[\pi(t\text{-}6)/12]$, respectively. Fig. 1 demonstrates clearly that the evolution of small clusters leads, as $[H_2SO_4]$ increases, to the nucleation and growth of nanoparticles. Under the condition studied here the concentration of small positive ions peaks around 1 nm, while that of negative ions peak around 0.7 nm when $[H_2SO_4]> \sim 2\text{x}10^6\ \text{cm}^{-3}$. A mode of negative ions between 1-3 nm is clearly visible during the nucleation period, while there is no such a mode in the size spectrum of the positive ions. The nucleation on negative ions is more favorable under the given condition. There exists a pool of neutral clusters/ particles smaller than ~ 3 nm, which are resulted from the recombination of oppositely charged cluster ions. Due to the Kelvin effect, organics can condense only on the particles larger than ~ 3 nm. The obvious gap (~3-6 nm) in the number size distributions of positively and negatively charged clusters/particles shown in Fig. 1a, b is associated with the activation of particles by organics and neutralization of charged particles.

Size-dependent charged fraction (CF) can be readily calculated based on the size distributions of positive, negative, and neutral clusters/particles simulated explicitly in our model. For the case shown in Figure 1, we find that there exists a minimum CF of ~ 2-3% during the nucleation period. The diameter (d_m) of minimum CF is ~ 2.5-7 nm for positive and ~4-8 nm for negative ions, respectively. The minimum is formed due to the neutralization of nanoparticles nucleated on ions and an increase in the charging probability with increasing particle size. For the case studied here (Fig. 1), particles from the size range between 2 and 4 nm are significantly negatively overcharged while they are only slightly positively overcharged.

The IMN nucleation rates (J_{IMN}) are calculated based on the net fluxes of particles across the critical size of neutral clusters. Figure 2 presents J_{IMN} as a function of time under nine different combinations of T, RH, $[H_2SO_4]$, Q, and S. $[H_2SO_4]$ and T are the two most important parameters controlling the particle formation. RH, Q, and S affect the nucleation rates at a lesser degree.

We have investigated IMN as a source of new particles in the atmosphere, using a global 3-D chemical transport model (Harvard GEOS-Chem: http://www.as.harvard.edu/chemistry/trop/geos/index.html) coupled with a nucleation sub-model. Our study indicates that IMN contributes to new particle formation not only in the upper atmosphere but also in the lower atmosphere. The temporal and 3-D spatial distributions of IMN rates will be discussed.

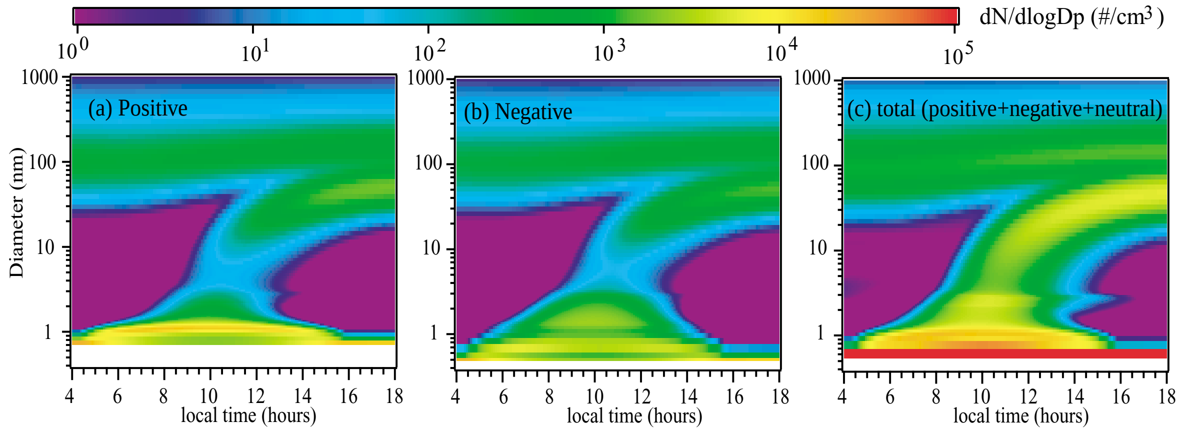

Figure 1. Evolution of clusters /particles: (a) positively charged, (b) negatively charged, and (c) total. T= 280 K and RH= 50%.

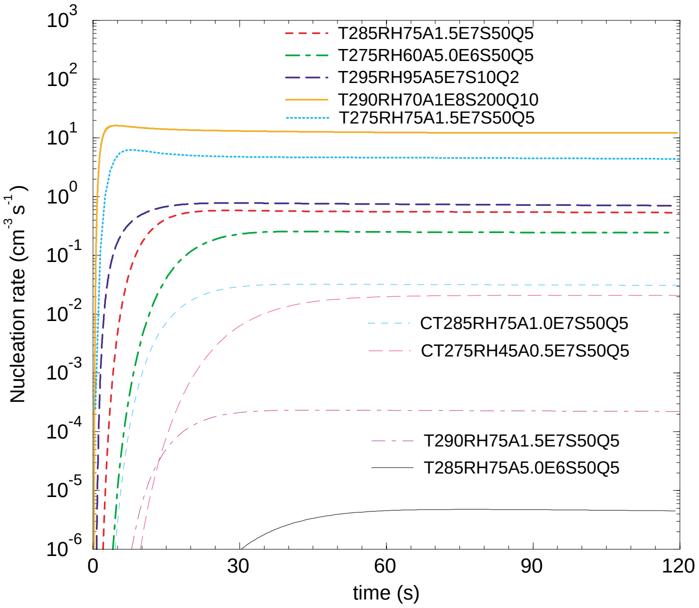

Figure 2. Ion-mediated nucleation rates as a function of time under nine different combinations of temperature (*T*), relative humidity (*RH*), [H_2SO_4], ionization rate (*Q*), and surface area of preexisting particles (*S*). Read T285RH75A1.5E7S50Q5 as the case with *T* of 285 K, *RH* of 75%, [H_2SO_4] of 1.5×10^7 cm^{-3}, surface area of 50 $\mu m^2/cm^3$, and ionization rate of 5 ion-pairs $cm^{-3}s^{-1}$. For high [H_2SO_4] (up to ~10^8 cm^{-3} in polluted areas), IMN can lead to a significant particle nucleation even if the ambient temperature *T* is ~ 290 K. When [H_2SO_4] is ~ 1.5×10^7 cm^{-3}, *T* = 275 K can lead to high nucleation rates at *RH*>~75%. When [H_2SO_4] is ~ 5 $\times 10^6$ cm^{-3}, *T* < 275 K and RH above 60% lead to a noticeable nucleation (>0.1 $cm^{-3}s^{-1}$).

CONCLUSIONS

Ions, which are generated in the atmosphere by galactic cosmic rays and other ionization sources, may play an important role in the formation of atmospheric aerosols. Results obtained using the second generation IMN model, in which the most recent thermodynamic data for neutral and charged H_2SO_4-H_2O clusters were used, suggest that ion-mediated nucleation of H_2SO_4-H_2O can lead to significant production of new particles not only in the upper atmosphere but also in the lower atmosphere.

Keywords: *Nucleation mechanism, Ion-mediated Nucleation, Kinetic modelling, Charged Fractions, Nanoparticle, Global Aerosol Modeling.*

REFERENCES

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: A review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Yu, F. (2006a) Effect of ammonia on new particle formation: A kinetic H_2SO_4-H_2O-NH_3 nucleation model constrained by laboratory measurements, *J. Geophys. Res.*, 111, doi:10.1029/2005JD005968.

Yu, F. (2006b) From molecular clusters to nano-particles: Second-generation ion-mediated nuclea-tion model, Atmos. Chem. Phys. Disc., 6, 3049-3092, 2006.

This work was supported by the NSF under grant ATM 0618124 and by the NOAA/DOC under grant NA05OAR4310103.

Contribution of ion-induced nucleation on Tropospheric nucleation

Lauri Laakso, Anne Hirsikko, Stéphanié Gagné, Miikka Dal Maso and Markku Kulmala
Department of Physical Sciences, University of Helsinki, P.O.BOX 64, FI-00014, Finland

INTRODUCTION

New particle formation is taking frequently place in the global atmosphere worldwide (Kulmala et al, 2004). Despite many observations, however, the exact nucleation mechanism still remains an open question. Several nucleation pathways, including an ion-induced, ternary, binary and kinetic nucleation, have been proposed, but the relative importance of these processes in different environments is still unknown. Ternary and binary nucleation refers to the number of vapours participating in the nucleation process, whereas ion-induced nucleation refers to the presence of charges in nucleation (Weber at al., 1996; Laakso et al., 2002). Thus, both binary and ternary nucleation can be either ion-induced or neutral. A recently-proposed particle formation mechanism is the activation of stable clusters which can involve either neutral or ion clusters (e.g. Kulmala et al., 2006).

The main difficulty in identifying atmospheric nucleation mechanism arises from experimental problems: charged particles of any size can be measured with different kind of ion-spectrometers, whereas neutral particles smaller than 3 nm in diameter can not typically be measured (for recently developed techniques, see Riipinen et al. elsewhere in this volume). This is problematic, since nucleation take place in sizes of around 1-2 nm. As a result, the only way to get information on the initial steps of the particle formations is to measure the concentrations of trace gases, ions, and particles larger than 3 nm in diameter, and then to combine these measurements with sophisticated model simulations.

In this study we show results from two different methods which are used for investigating the importance of ion-induced nucleation on Tropospheric particle formation. The first method is based on combination of measurements and model simulations whereas the second method on the charging state of atmospheric aerosol particles.

METHOD I:
AEROSOL AND ION MEASUREMENTS AND MODEL SIMULATIONS

The investigations are based on long-term measurements carried out at Hyytiälä measurement station in Central Finland. The measurements were done by DMPS, two different ion spectrometers and ionizing radiation measurements (Laakso et al., 2004). In addition to measurements, we utilized charged aerosol particle and ion model in the interpretation of the results.

Since we wanted to minimize the number of open parameters in model calculations, we used for the model input as much observational data as possible. Observational input data include growth rates, pre-existing particle concentration, cluster ion concentration, temperature and relative humidity.

We did more than 500 runs for each day with the model AEROION (Laakso et al., 2002). The results were compared with the observations by minimizing the least-square displacement between the observed and simulated particle and ion concentrations in the growing nucleation mode.

Altogether 64 new particle formation episodes for one full calendar year (April 2003-April 2004) were simulated.

METHOD II:
AEROSOL PARTICLE CHARGING STATE MEASUREMENTS

We developed a new DMPS-setup (Laakso et al., 2004, 2006) which operates as a conventional DMPS, but with two modifications:

1) Electric field in DMA can be switched between positive and negative polarity
2) Aerosol particle charger can be switched on and off

This modification allows us to calculate the ration between naturally charged particles and particles in forced bipolar equilibrium. This ratio gives information on the nucleation mechanism. If the naturally-charged particles carry fewer charges than the particles charged in equilibrium, the neutral nucleation mechanism dominates. On the other hand, excess of charges indicates contribution of ion-induced nucleation. In this study we used data from the period April 2005-June 2005.

RESULTS

Both methods gave consistent results: during most of the time, neutral nucleation mechanisms dominate. Both methods gave relative low ion induced nucleation fractions. Median values for Method I are 3% for negative and 1% for positive ion-induced nucleation whereas for Method II they are 0.25% and 0.1%.

However, despite these low values, with low total nucleation rates and cold weathers around and below

0°C the picture is different and ion-induced nucleation may produce most of the new particles. Figure 1 shows the contribution of ion-induced nucleation as a function of temperature based on method I.

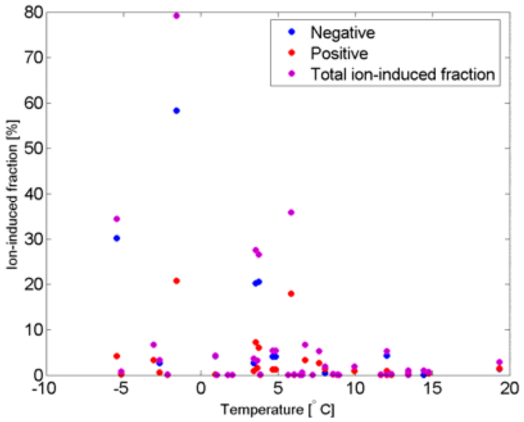

Figure 1: Fraction of ion-induced nucleation of total nucleation rate as a function of temperature based on the Method I.

CONCLUSIONS

We have calculated the contribution of ion-induced nucleation on new particle formation in a boreal forest based on two different methods. Both methods gave consistent results and showed that typically, ion-induced nucleation was less important. However, with low temperatures, the contribution of ion-induced nucleation was found to be significant.

Keywords: *New particle formation, ion-induced nucleation, atmospheric nucleation*

REFERENCES

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, *J. Aerosol Sci.*, 35, 143–176, 2004.

Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration, *Atmos. Chem. Phys.*, 6, 787–793, 2006.

Laakso, L., Mäkelä, J., Pirjola, L., and Kulmala, M.: Model studies on ion-induced nucleation in the atmosphere, *J. Geophys. Res.* D, 107, 4427, 10.1029/2002JD, 2002.

Laakso, L., T. Anttila, K. E. J. Lehtinen, P. P. Aalto, M. Kulmala, U. Hõrrak, J. Paatero, M. Hanke, F.Arnold, Kinetic nucleation and ions in boreal particle formation events, *Atmos. Chem. Phys*, Page(s) 2353-2366. SRef-ID: 1680-7324/acp/2004-4-2353, 2004

Lauri Laakso, Stéphanie Gagné, Tuukka Petäjä, Anne Hirsikko, Pasi. P. Aalto, Markku Kulmala, Veli-Matti Kerminen, "Detecting charging state of ultra-fine particles: instrumental development and ambient measurements, *Atmospheric Chemistry and Physics Discussions*, 6, 1–29, 2006

Weber, R. J., Marti, J., McMurry, P. H., Eisele, F., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle formation rates: implications for nucleation mechanisms, *Chem. Eng. Comm*, 151, 53–64, 1996.

Experimental Study of Heterogeneous Nucleation on Charged and Uncharged Nanoclusters

Paul M. Winkler, Gerhard W. Steiner, Georg P. Reischl, Aron Vrtala, Paul E. Wagner
Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria
Anca Hienola, Hanna Vehkamäki, and Markku Kulmala
Department of Physical Sciences, University of Helsinki, P.O. Box 64, FIN-00014 University of Helsinki, Finland

INTRODUCTION

In recent years formation and properties of nano-particles have received increasing attention. Formation of new atmospheric nano-particles can lead to a substantial increase of atmospheric particle number concentration and is relevant in connection with the evolution of global climate.

In this study, we investigated the dynamics of the initial activation and growth of nano-particles, both charged and uncharged (neutralized). An organic vapour compound (n-propanol) was allowed to condense on WO_x seed particles via initial activation by heterogeneous nucleation. We considered seed particles with diameters down to about 1.4 nm. In this size range no quantitative experimental data on heterogeneous nucleation are available so far. The results may have significant implications for the phase transitions on nano-particles, especially concerning mechanisms of atmospheric aerosol formation.

EXPERIMENTAL PROCEDURE

The experimental system – shown schematically in Fig. 1 – includes a source of monodispersed particles and a vapour generation unit. Vapour supersaturation is achieved by adiabatic expansion in a computer controlled thermostated expansion chamber, the size analyzing nuclei counter (SANC). Droplet growth is observed using the constant-angle Mie scattering (CAMS) detection method (Wagner, 1985). Details of the experimental system are presented elsewhere (Wagner *et al*., 2003).

Generation of seed particles was performed with a newly developed WO_x-Generator. Thereby, tungsten oxide sublimates into the surrounding purified carrier gas flow passed through the generator. Primary produced molecules subsequently grow to larger clusters by coagulation. Using a newly developed differential mobility analyzer (Nano-DMA) well-defined unipolarly charged monodispersed particles were extracted. Typically, after passing the Nano-DMA particles are brought into charge equilibrium by means of a radioactive source in a neutralizer. However, by replacing such a neutralizer with corresponding dummy particles undergo practically the same diffusion losses but stay charged. By switching the polarity of the Nano-DMA electrode we obtained negatively and positively charged particles, respectively. The nucleation behavior on such cluster-ions compared to neutral nano-clusters was investigated. The size distribution of the particles obtained was monitored by a newly developed differential mobility particle spectrometer system (Nano-DMPS) allowing to analyze in the diameter range from 0.5 to 40 nm. Nearly lognormal size distributions were found with mean particle diameters ranging from 1.4 to 4 nm and geometric standard deviations between 1.08 and 1.12. Particle number concentrations around 5000 cm^{-3} were observed.

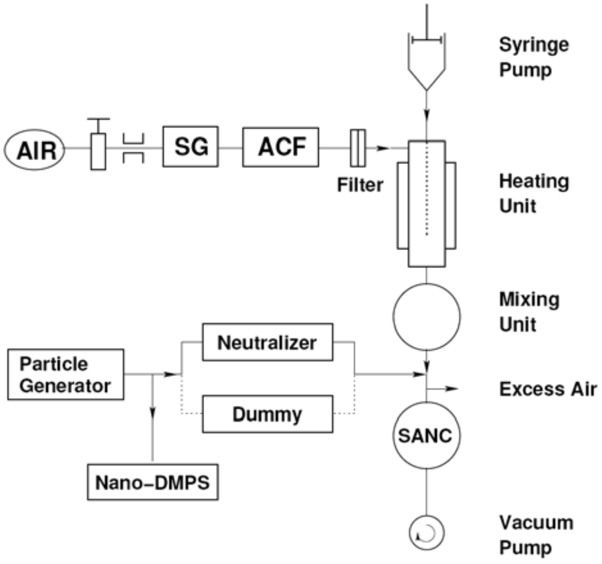

Figure 1. Schematic diagram of experimental system. SG: Silica gel gas drier, ACF: Active carbon filter, SANC: Size analyzing nuclei counter.

n-Propanol vapour was added to the system by controlled injection of a liquid beam and subsequent quantitative evaporation in a heating unit. In order to achieve the desired vapour supersaturations, a well-defined binary vapour-air mixture together with the seed particles were passed into a thermostated expansion chamber. During a computer controlled measurement cycle, the chamber was subsequently connected to a low pressure buffer tank resulting in adiabatic expansion with expansion times around 8 ms and well-defined vapour supersaturations were obtained. Temperature and vapour phase activity after expansion were determined using Poisson's law.

Those particles inducing heterogeneous nucleation at the vapour saturation ratios considered lead to the formation and growth of liquid droplets. Using the CAMS detection method (Wagner, 1985), the radius and number concentration of the growing droplets can be determined simultaneously at various times during the growth process without any external calibration.

RESULTS

Using the SANC we have measured the number concentration of droplets heterogeneously nucleated by charged and uncharged WO_x particles at various vapour saturation ratios and at constant nucleation temperature. At low supersaturations no particles are activated, whereas with increasing supersaturation more and more particles will be activated and grow to detectable sizes. Beyond a certain saturation ratio all particles are activated and typically no further increase of the particle number concentration is observed. Thereby we obtained the heterogeneous nucleation probability, i.e., the number concentration of activated droplets normalized relative to the total concentration of seed particles. In Figure 2, corresponding heterogeneous nucleation probabilities are plotted for negatively and positively charged particles and for uncharged particles, respectively. Solid lines are fitted to the data points to guide the eye. As can be seen from this figure, particles of same size but different charging state exhibit different nucleation behaviour. Obviously, negatively charged WO_x particles are more easily nucleated to growth than positively charged particles and neutral ones. Smaller saturation ratios are generally required to see charged particles being nucleated. Heterogeneous nucleation probabilities do not exceed unity, however, this figure shows several data points at high saturation ratios, where a steep increase beyond unity is observed. This is related to the onset of homogeneous nucleation. As can be seen from Figure 2, for neutral clusters homogeneous nucleation clearly starts at lower nominal vapour saturation ratios than for the case of charged particles. Due to the slower activation of neutral clusters less vapour is depleted which may cause homogeneous nucleation to start earlier than for charged particles. As a consequence the detection limit for neutral particles was found to be around 1.75 nm whereas negatively and positively charged particles allowed being detected at a diameter as low as 1.4 nm.

CONCLUSIONS

In this study we have for the first time performed heterogeneous nucleation experiments using charged and uncharged seed particles with diameters ranging from 1.4 nm to 4 nm. Thereby, we observed that nucleation on charged particles is clearly enhanced compared to neutral particles. For n-propanol vapour the charge effect on nucleation becomes evident considering seed particle diameters below 4 nm. For comparison, similar experiments for different vapours like, e.g., water or n-nonane vapour are planned.

From the viewpoint of atmospheric aerosols and their climate interaction our new observation concerning the nucleation behaviour of charged and uncharged particles clearly shows that ion-induced nucleation is an additional process likely to cause atmospheric new particle formation. In fact, recent findings by Laakso et al. (2006) indicate that ion-induced nucleation frequently does occur in the atmosphere. Consequently, for more accurate representation of organic aerosol formation processes ion-induced nucleation should be accounted for in global climate prediction models.

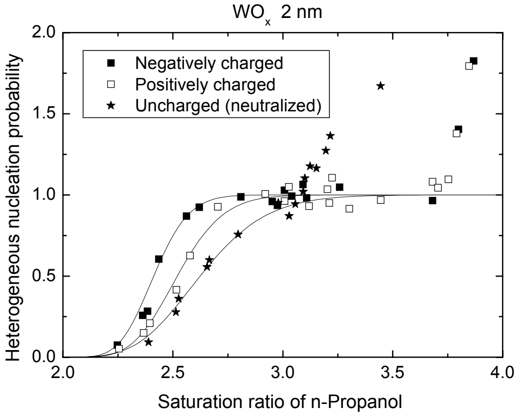

Figure 2. Heterogeneous nucleation probabilities for n-propanol on WO_x particles of different charging state.

Keywords: *Nano-particle, Heterogeneous Nucleation, n-Propanol, charged particle*

REFERENCES

Laakso, L., Gagné, S., Petäjä, T., Hirsikko, A., Aalto, P. P., Kulmala, M., and Kerminen, V.-M., (2006) Detecting charging state of ultrafine particles: instrumental development and ambient measurements, *Atmos. Chem. Phys. Discuss*, **6**, 6401-6429.

Wagner, P. E. (1985) A constant-angle Mie scattering method (CAMS) for investigation of particle formation processes, *J. Colloid Interface Sci.*, **105**, 456-467.

Wagner, P. E., Kaller D., Vrtala, A., Lauri, A., and Kulmala M. (2003) Nucleation probability in binary heterogeneous nucleation of water-n-propanol vapour mixtures on insoluble and soluble nano-particles, *Phys. Rev.,* **E67**, 021605:1-12.

This work was supported by the Austrian Science Foundation (FWF, Project No. P16958-N02).

Ari Laaksonen[1,2], Santtu Mikkonen[1], Antti-Pekka Hyvärinen[2], Kari Lehtinen[1,2], Sanna-Liisa Sihto[3] and Markku Kulmala[3]
[1]Department of Physics, University of Kuopio, P.O. Box 1627, 70211, Kuopio, Finland
[2]Finnish Meteorological Institute, P.O. Box 503, FI-00101, Helsinki, Finland
[3]Department of Physical Sciences, University of Helsinki, P.O. Box 64, FI-00014, Helsinki, Finland

INTRODUCTION

Atmospheric nucleation is likely to proceed via clustering of sulphuric acid molecules with possible association of species such as water, ammonia and oxidation products of volatile organic compounds. Such a process is extremely difficult to study either experimentally or theoretically. However, methods are available for inferring information on the compositions of critical nuclei from aerosol and gas-phase measurements taken during atmospheric nucleation events. Here, we present results obtained during the 2003 QUEST 2 campaign in Hyytiälä, Finland.

MATERIALS AND METHODS

All the data studied in this work was measured in Hyytiälä, southern Finland, during March-April, 2003. The data covers 15 nucleation events, during which aerosol size spectra and concentrations of sulphuric acid and ammonia, together with several other trace gases, were measured in 10 minute intervals. The formation rate of 3 nm particles was evaluated from increases of 3-26 nm particles during the events, and the nucleation rates of 1 nm particles were calculated based on the 3 nm formation rates, taking into account particle growth rates between 1 and 3 nm (based on time shift between increase of sulphuric acid and 3-6 nm particle concentrations) and the condensation sink.

The molecular contents of the critical nuclei can be studied with the aid of the nucleation theorem, a very general relation which states that the number of molecules of a given species in the nucleus can be obtained from the slope of the logarithm of the nucleation rate as a function of the logarithm of the gas-phase concentration of that species. In this way, it has been found that in atmospheric nucleation events, critical nuclei are likely to contain 1-2 sulphuric acids. However, there usually is considerable scatter in the data, at least partially caused by the fact that other variables effecting the nucleation – i.e. temperature, and the concentrations of other participating species – are not constant during the events. Here, we use an alternative approach to study the contents of the critical nuclei. Instead of simply making linear best fits of ln(J) vs ln[H_2SO_4] and other gases, we used a nonlinear multivariate regression analysis.

Before performing the regression analysis, we studied the data using a self organizing map (SOM). The SOM separated the data to two clusters according to temperature, one cluster corresponding to negative and the other to positive temperatures, which was taken into account in constructing the regression model. The form of the regression model is suggested by nucleation theory.

RESULTS AND DISCUSSION

The model producing the best total coefficient of determination is

$$\log(J) = \beta_0 + \left(\beta_{1+} + \beta_{1-}\right)\log(H_2SO_4) + \left(\beta_{2+} + \beta_{2-}\right)\log(NOx) + \left(\beta_{3+} + \beta_{3-}\right)\log(NH_3) + \left(\beta_{4+} + \beta_{4-}\right)\log(H_2O) + \varepsilon,$$

where β_0 is the intercept, $\beta_1,\ldots,\ \beta_4$ are the regression coefficients and ε describes the zero-mean normally distributed and uncorrelated error terms. NO_x denotes gas phase concentration, and the other quantities inside the logarithms are gas-phase activities of the respective species. As suggested by the self-organising map analysis in which the data was seen to separate into two clusters distinguished by temperatures below and above freezing, respectively, the regression coefficients $\beta_1,\ldots,\ \beta_4$ were taken to depend on the temperature such that the slopes are different for temperatures of below and over 0°C. This division improved the statistical significance of the model. The model was used for both 1 nm (J_1) and 3 nm (J_3) particle formation rates. The number of observations in the model was N = 257 for J_1 and $N = 184$ for J_3.

The results of the regression analysis are given in the following tables:

	β-	β-
H2SO4	1.3	1.2
NH3	-0.1	0.3
H2O	-1.7	-1.8
NOx	0.7	-0.3

Table 1. Regression coefficints for the J_3- model.

	β-	β-
H2SO4	1.4	0.6
NH3	0.7	1.1
H2O	1.3	1.5
NOx	0.2	2.6

Table 1. Regression coefficints for the J_3- model.

CONCLUSIONS

Our results suggest that the critical nuclei contain roughly one sulphuric acid, one ammonia, and 1-2 water molecules. The fact that including nitrogen oxides in the regression model clearly improved the total coefficient of determination is rather puzzling, and could sign the participation of NO_x in some key reactions leading to formation of nucleating and/or condensing species. Interestingly, water has a boosting effect on 1 nm particle formation but hinders the 3 nm formation. A possible explanation is the effect of relative humidity on the size of the coagulation sink through growth of deliquescent pre-existing particles, whereby cluster scavenging before they reach the 3 nm size would be higher at higher relative humidities. The total coefficients of determination are 0.56 for J_3 and 0.77 for J_1, indicating that there may be still some unidentified chemical species participating in the nucleation. J_3-

Homogeneous nucleation rate measurements and the properties of small water clusters

Barbara E. Wyslouzil[1], **Yoojeong Kim**[2], **Gerald Wilemski**[3], **Judith Wölk**[4], **and Reinhard Strey**[4]
[1]*Department of Chemical and Biomolecular Engineering, Ohio State University, Columbus OH, 43210 USA*
[2]*Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester MA 01609-2280 USA*
[3]*Department of Physics, University of Missouri – Rolla, Rolla MO, 65409 USA*
[4]*Institut für Physikalische Chemie, Universität zu Köln, Köln, Germany*

INTRODUCTION

Water droplet formation and growth plays a key role in natural and technological settings including, for example, cloud formation and power generation in steam turbines. Some of the earliest experimental work dates back to C.T. R. Wilson (1897) who used a simple expansion cloud chamber to probe the limits of supersaturation that could be attained by dust free moist air without condensation. Yet, despite more than 100 years of experimental and theoretical work, quantitative prediction of water nucleation rates J over a wide range of temperature T and supersaturation S is still difficult. This paper summarizes our efforts to measure the nucleation rates of water and to use these rates to determine the properties of the critical clusters, i.e., the smallest fragments of the new phase that are metastable in the supersaturated vapour. These data are critical to test and develop robust theories of nucleation for use in atmospheric models.

EXPERIMENTAL NUCLEATION RATES

Nucleation rates can now be measured over ~ 20 orders of magnitude by combining data from a wide variety of techniques including the thermal diffusion cloud chamber ($10^{-3}<J/\text{cm}^{-3}\text{s}^{-1}<10^{2}$) (Heist and Reiss, 1973), laminar flow diffusion tube reactor ($10^{4}<J/\text{cm}^{-3}\text{s}^{-1}<10^{7}$) (Mikheev *et al.*,2002) nucleation pulse chamber ($10^{6}<J/\text{cm}^{-3}\text{s}^{-1}<10^{9}$) (Wolk and Strey,2001), and supersonic nozzle ($10^{16}<J/\text{cm}^{-3}\text{s}^{-1}<10^{18}$) (Kim *et al.*,2004). In each of these devices the characteristic time Δt, temperature, and supersaturation corresponding to the maximum nucleation rate is determined either directly from the experiment or by modeling the flow. A particle detection technique, such as light, neutron, or x-ray scattering yields the number concentration N of the aerosol that formed during the nucleation burst. The experimental nucleation rate J is then simply $J=N/\Delta t$.

Figure 1 illustrates that the nucleation rates measured for both isotopes of water in three of these devices are remarkably consistent over ~12 orders of magnitude. An interesting finding of Wölk and Strey (2001) was that the measured nucleation rates for H_2O and D_2O superimpose when plotted as a function of S.

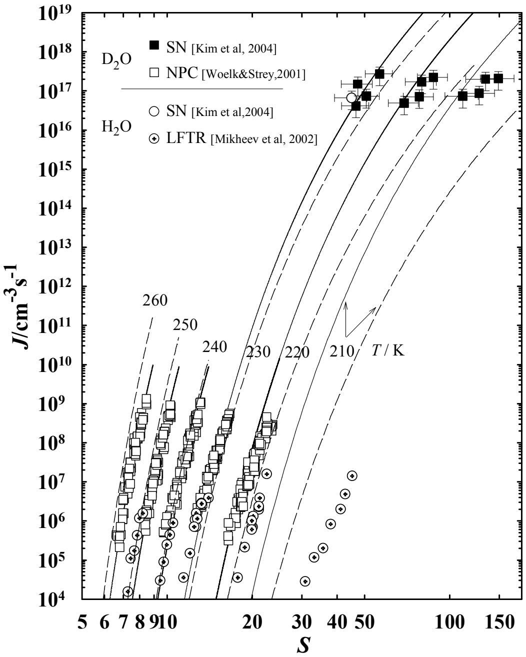

Figure 1. Isothermal nucleation rates of D_2O, measured in supersonic nozzles (SN) are compared to nucleation rate measurements made in the nucleation pulse chamber (NPC). The dashed lines are the predictions of Eq.(1). The solid lines are the predictions of the empirical function for the nucleation rate of D_2O that Wölk and Strey (2001) developed using the NPC data. A single H_2O nucleation rate measured in a nozzle is also shown, as are the H_2O nucleation rates measured by Mikheev *et al.* (2002) in the laminar flow tube reactor (LFTR). The H_2O nucleation rates from the NPC lie directly on top of the D_2O rates and are not shown.

NUCLEATION THEORY AND CORRECTIONS

Despite its limitations, classical nucleation theory (CNT) is still used as a baseline with which to compare experiments. In the Becker-Döring formulation the nucleation rate is given by,

$$J = K\exp(-\Delta G^* / kT) \qquad (1)$$

where K is the kinetic prefactor, ΔG^* is the free energy of the critical cluster, and k is the Boltzmann constant. Since only bulk material properties are required to evaluate Eq(1), it is extremely easy to use. As illustrated in Figure 1, it even reproduces the measured nucleation rates near T= 240 K quite well, although further examination shows that the temperature dependence of Eq. (1) is too strong. For both isotopes of water, simple temperature dependent correction factors have been developed (Wölk and Strey, 2001) that appear to be quite robust even when extended far beyond the region for which they were determined.

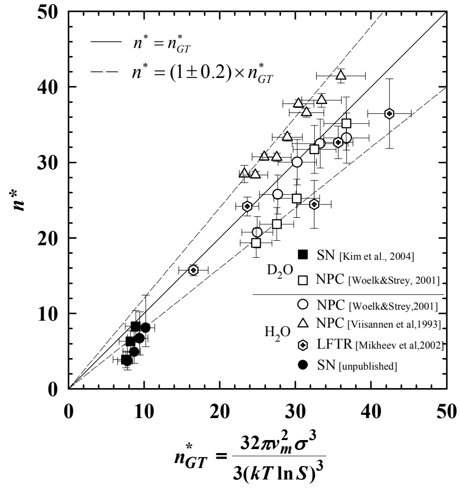

Figure 2. The experimental values of *n** are compared to the predictions of the Gibb's Thompson equation n^*_{GT}. The bulk physical properties of water (molecular volume ν, surface tension σ) were used to evaluate n_{GT}.

PROPERTIES OF THE CRITICAL CLUSTERS

If measured nucleation rates are accurate enough, we can determine the properties of the critical clusters, in particular the number of molecules in the critical cluster, *n**, and the excess internal energy of the critical cluster, $E_x(n^*)$. For nucleation of a single species, the first nucleation theorem (Kaschiev, 1982) states

$$\left(\frac{d(\ln J)}{d(\ln S)}\right)_T \cong n^*, \tag{2}$$

while the second (Ford,1997) states

$$\left(\frac{d(\ln J)}{dT}\right)_{\ln S} \cong \frac{1}{kT^2}\left[L - kT + E_x(n^*)\right], \tag{3}$$

where *L* is the latent heat of the bulk liquid.

Figures 2 and 3 summarize the critical cluster properties measured by applying Eqs. (2) and (3) to the nucleation rate data. The experimental values of *n** are within ±20% of those predicted by the Gibbs-Thomson equation for clusters containing as few as 6 – 8 molecules. Even the excess internal energies appear to be in reasonable agreement with the predictions of classical theory and extrapolated bulk physical properties down to the same size range.

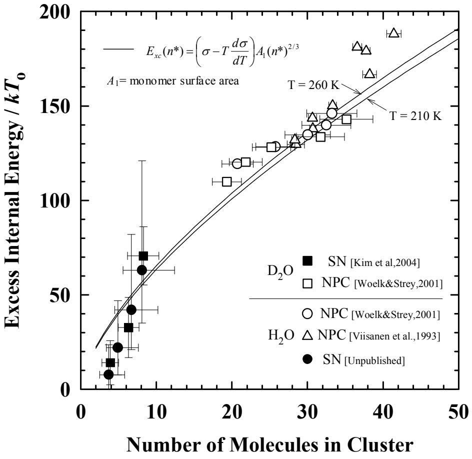

Figure 3: The experimental values of $E_x(n^*)$ are compared to the predictions of classical nucleation theory for D_2O at T = 260 K and 210 K. The lines for H_2O are essentially the same.

CONCLUSIONS

Given the extreme sensitivity of nucleation rate measurements, the consistency between data sets determined using very different experimental systems is remarkable. Although Eq.(1) predicts the homogeneous nucleation rates for water at 240K quantitatively, the temperature dependence is incorrect, a fact that leads to discrepancies of orders of magnitude in rate at other temperatures. The nucleation rate measurements furthermore provide the number of molecules in the critical cluster and its excess energy. For water these values are in surprisingly close to the theoretical predictions of the classical nucleation theory down to rather small cluster sizes.

Keywords: *nucleation rates, water cluster properties, aerosol formation*

REFERENCES

Ford, I. (1997), Nucleation theorems, the statistical mechanics of molecular clusters, and a revision of classical nucleation theory, *Phys. Rev. E.*, *56*, 5615.

Heist, R. and Reiss, H., (1973) Investigation of the homogeneous nucleation of water vapor using a diffusion cloud chamber, *J. Chem. Phys.* 59**,** 665.

Kaschiev, D. (1982) On the relation between nucleation work, nucleus size, and nucleation rate, *J. Chem. Phys.*, 76**,** 5098.

Kim, YJ, Wyslouzil, BE, Wilemski,G, Wölk, J, and Strey, R. (2004) Isothermal Nucleation Rates in Supersonic Nozzles and the Properties of Small Water Clusters, *J. Phys. Chem. A*, 108, 4365.

Mikheev, V.B., Irving, P.M., Laulainen, N.S., Barlow, S.E., Pervukhin, V.V. (2002) Laboratory measurement of water nucleation using a laminar flow tube reactor *J. Chem. Phys.* 116, 10772

Viisanen, Y., Strey, R., and Reiss, H. (1999) Homogeneous nucleation rates for water *J. Chem. Phys.* 99, 4680; (2000) 112, 8205.

Wölk, J. and Strey, R. (2001) Homogeneous Nucleation of H_2O and D_2O in Comparison: The Isotope Effect., *J. Phys. Chem.* 105, 11683.

This work was supported by the NSF under Grants CHE-0410045 & CHE-0518042, and by the Donors of the Petroleum Research Fund administered by the American Chemical Society.

Ternary Nucleation Mechanisms and New Particle Formation

Robert McGraw
Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, NY, 11973

INTRODUCTION

Recent kinetic extensions of the nucleation theorem (KNT) suggest that the logarithm of the steady-state nucleation rate has strong multi-linear dependence on the log concentrations of condensable species present in the vapor phase. A further remarkable result is that the coefficients of this linear dependency provide a direct determination of the molecular content of the critical nucleus itself.

The new approach is applied to recent measurements by Zhang and co-workers on the p-toluic acid/ sulfuric acid/water ternary vapor system. A linear minimum variance parameterization for nucleation rate dependence on vapor composition, accurate over the range of the measurements, is obtained. Estimates of critical nucleus composition are also presented. These show that a single molecule of p-toluic acid present in the critical nucleus is sufficient to trigger a ternary nucleation event.

Current research is focused on the mechanisms and rates by which critical nuclei (particles of about 1nm in size), once formed, reach climate-significant size.

TERNARY NUCLEATION MECHANISM

The work described here was carried out in collaboration with Renyi Zhang at Texas A&M (Zhang et al., 2006; McGraw and Zhang, 2006). Analysis here will focus on the ternary system p-toluic acid/sulfuric acid/water to illustrate the new methods, which enable characterization of the critical nucleus and parameterization of the nucleation rate for use in models.

There is a strong propensity, at least locally on the nucleation rate surface, for the nucleation rate to be a multilinear function of vapor species concentrations and temperature when all variables are cased in appropriate form. From the kinetic nucleation theorem (McGraw and Wu, 2003), we find:

$$\ln J \approx \ln J_0 + \sum_i (g^*_i + \delta_i)(\ln n_i - \ln n_i^{\,0}) - \frac{\Delta E(g^*_1, g^*_2, \cdots)}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (1)$$

where J is the nucleation rate, n_i is the vapor phase concentration of species i , g^*_i is the number of molecules of species i in the critical nucleus, δ_i is a small kinetic factor (between 0 and 1), ΔE is the energy required to form the critical nucleus (having the specified composition) from the vapor, k is the Boltzmann constant and T is temperature. According to Eq. 1, a multilinear analysis of nucleation rate measured as a function of vapor composition and temperature can provide a direct determine of critical nucleus properties – molecular content and cluster energy. The Zhang et al. measurements are at constant temperature, so only the first terms in Eq. 1 are significant and the cluster energy cannot be determined. Furthermore the measurements are at constant relative humidity, and so the water content of the critical nucleus cannot be determined. This leaves the three variables: J , and vapor phase concentrations of organic and sulfuric acids.

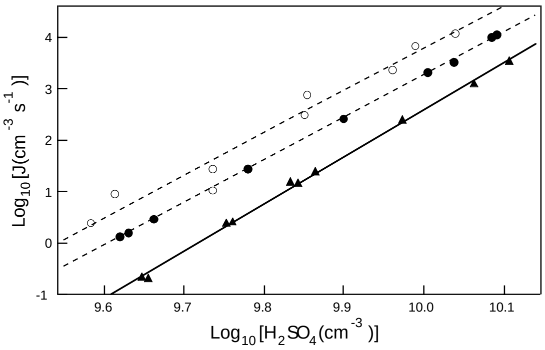

Figure 1. Measurements from Zhang et al. (2004) for the ternary system system p- toluic acid/sulfuric acid/water plotted in nucleation theorem modivated coordinates, log nucleation rate (J) versus log sulfuric acid vapor concentration. Filled circles, p-toluic acid concentration = 0.2ppb. Open circles, p-toluic acid concentration = 0.4ppb. Triangles, binary sulfuric acid-water measurements. Solid line, least-squares fit to the binary data. Dashed lines, projections from the linear minimum variance estimator (LMVE) plane (Eq. 2) evaluated at the two p-toluic acid concentrations (these parallel lines live on the same plane and when projected, as shown here, have the same slope).

The figure shows conformity to Eq. 1 for these remaining three variables. Under ternary conditions, the measurements are expected to lie on a 2D plane in the 3D coordinate space, and it is clear from Fig. 1 that they do ($R^2 = 0.98$). The planar fit takes the simple form:

$$z = -76.75 + 8.12x + 1.86y \qquad (2)$$

where $z = Log_{10}[J_T, cm^{-3}s^{-1}]$, $x = Log_{10}[H_2SO_4, molecules\ cm^{-3}]$, and $y = Log_{10}[Organic,\ ppb]$ for the ternary nucleation rate. Comparison of Eqs. 1 and 2 immediately yields a critical nucleas composition of 8 molecules of sulfuric acid and just a single molecule of the organic acid. Other ternary systems that we have examined of this type – having only different organic acids – show a similar trend. Namely, just a single molecule of the organic acid is present in the critical nucleus, along with a similar number (about 8) molecules of sulfuic acid. Measurements on the benzoic acid system at two different values of the RH furnish a crude estimate of the water content – we estimate about 17 molecules of water present in the critical nucleus, but there is large uncertainty to this last value.

NEW PARTICLE FORMATION

Figure 1 presents a bit of a paradox when compared with atmospheric measurements of new particle formation. Specifically the relative rate sensitivities $\partial Log_{10} J / \partial Log_{10}[H_2SO_2]$ as measured in the lab are much higher than in the field. Thus we observe a slopes of 9 and 8 for the binary and ternary rates, respectively, compared with observations at Mauna Loa, HI, and Idaho Hill, CO, which found values only between 1 and 2 [Eisele and McMurry, 1997]. We are currently investigating this discrepancy and will report preliminary results along with a method of moments analysis of the mechanisms and rates by which critical nuclei (particles of about 1nm in size), once formed, reach climate-significant size.

Keywords: *Nucleation, new particle formation, kinetic nucleation theorem*

REFERENCES

Eisele, F. L. and McMurry, P. H. (1997). *Recent progress in understanding particle nucleation and growth,* Phil. Trans. R. Soc. Lond. B 352, 191-201.

McGraw, R. and Zhang, R. (2006). *Multivariate analysis of homogeneous nucleation rate measurements: I. Nucleation in the p-toluic acid/sulfuric acid/water system,* in preparation.

McGraw, R. (2006). *Multivariate analysis of homogeneous nucleation rate measurements: II Temperature and vapor composition dependence,* in preparation.

McGraw, R. and Wu D. (2003). *Kinetic extensions of the nucleation theorem,* J. Chem. Phys. 118, 9337-9347.

Zhang, R., Zhao, J., Suh, I., Kholizov, A., McGraw, R., Molina, L. T. and Molina, M. J. (2006). *Characterization of the critical nucleus of blue haze,* in preparation.

This work was supported by the U. S. Department of Energy Atmospheric Sciences Program under Contract NO. DE-AC02-98CH1-886

Atmospheric Nucleation Rates From Laboratory Measurements of Molecular Clusters

Dave R. Hanson[1*] **and E. R. Lovejoy**[2,3]
[1]*Department of Chemistry, Augsburg College, Minneapolis, MN, USA*
[2]*Vermont, USA*
[3]*NOAA Aeronomy Lab, Boulder, CO, USA*

INTRODUCTION

The results from recent measurements of $(H_2SO_4)_n(H_2O)_m$ clusters have been interpreted in terms of providing nucleation rates (or upper limits to them) that are applicable to the free troposphere. These results provide an important benchmark for theory (Oxtoby, 1994; Vehkamaki, 2002) and for 'classical' laboratory experiments. The experimental procedure has been presented in detail previously (Hanson, 2002) and in this talk only a brief overview of the experiment and analysis will be presented. The talk will also discuss application to nucleation in the atmosphere such as comparison to ion-induced processes (Lovejoy, 2004) and the potential role of ammonia (Coffman, 1995.)

RESULTS and DISCUSSION

The results for the n = 2 cluster (the 'dimer' of H_2SO_4) could be readily interpreted by invoking equilibrium principles and thus an equilibrium constant (K_2) for the water mediated dimerization of H_2SO_4 monomers was derived. Also, the experimental conditions for some of the H_2SO_4 trimer (n= 3, any m) data showed it to be in equilibrium with the dimer + monomer (giving K_3.)

The dependencies of the cluster signals and the K_n on relative humidity (RH) were also studied. The dimer was weakly dependent on RH while the trimer and higher clusters had strong dependencies upon RH. Comparison with recent *ab initio* work (Ianni, 2000; Ding, 2003) on the n = 2 clusters indicates that the dimer contains roughly 5 water molecules (Ding, 2003.) This hypothesis is in seeming contradiction with the Nucleation theorem (Oxtoby, 1994) that states that the nucleation rate has a power dependency on a constituent that is equal to the number of molecules of that constituent in the critical cluster.

The results were included in a cluster growth model that included the equilibrium constants for each monomer addition/loss and the forward rate coefficient for addition of a monomer. Cluster growth times needed for this model were given by computational fluid dynamics simulations of the flow within the reactor. The forward rate coefficients were roughly half of the collisional growth rate coefficients. This translates into a reaction probability for addition of monomers to monomers and dimmers of 50 %.

Keywords: *Sulfuric acid, molecular cluster, water, nucleation*

Table 1. Thermodynamics and growth kinetics of the water mediated clusters containing *y* H_2SO_4.

$(H_2SO_4)_y(H_2O)_z$ [a]	ΔG^0, 242 K (kcal / mol) [b]	k_f (10^{-10} cm^3 /s) [c]
y = 2, dimer	-8.7 [d,e], -8.9 [f]	1.7
y = 3, trimer	-10.7 [d], -11.2 [e], <-11 [f]	1.8
y = 4, tetramer	< -12	2.0
y = 5, pentamer	< -12	2.2
y = 6, hexamer	< -12	2.4

[a] Summation over *z* for each species. [b] Free energy of formation of the hydrated y^th^-mer from the hydrated monomer and (y-1)th-mer. [c] Forward rate coefficient for formation of the yth-mer estimated from cluster growth model (see supplemental materials.) [d] 7 % RH. [e] 26% RH. [f] 53% RH.

REFERENCES

Oxtoby D. W., and Kaschiev, D., A general relation between the nucleation work and the size of the nucleus in multicomponent nucleation. *J. Chem. Phys*., 100, 7665-7671, (1994).

Vehkamaki, H., et al. An improved parameterization for sulfuric acid–water nucleation rates for tropospheric and stratospheric conditions. *J. Geophys. Res. D*, 107, 4622-4632, (2002).

Coffman, D.J., and Hegg, D.A, A preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer. *J. Geophys. Res.* 100, 7147-7160 (1995).

Lovejoy, E. R., Curtius, J. and Froyd, K. D., Atmospheric ion induced nucleation of sulfuric acid and water. *J. Geophys. Res. D*, 109, D8204, (2004).

Hanson, D.R., and Eisele, F.L. Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system. *J. Geophys. Res. D*, 107, (2002).

Ding, C-G, Laasonen, K., and Laaksonen, A., Two sulfuric acids in small water clusters. J. Phys. Chem. A, 107, 8648-8658 (2003).

Ianni, J. C., and Bandy, A. R., A theoretical study of the hydrates of $(H_2SO_4)_2$ and its implications for the formation of new atmospheric particles. *J. Mol. Struct. (THEOCHEM)* 497, 19-37 (2000).

Towards Observations of Neutral Atmospheric Clusters: Results from Hyytiälä, Southern Finland

Ilona Riipinen[1], Markku Kulmala[1], Hanna Manninen[1], Mikko Sipilä[1], Tuukka Petäjä[1], Genrik Mordas[1], Aadu Mirme[2], Marko Vana[1] Tuomo Nieminen[1], Lauri Laakso[1] and Veli-Matti Kerminen[3]
[1]Department of Physical Sciences, University of Helsinki, P.O. Box 64, FI-00014, Helsinki, Finland
[2]Institute of Environmental Physics, University of Tartu, Ülikooli 18, EE-50090, Tartu, Estonia
[3]Finnish Meteorological Institute, P.O. Box 503, FI-00101, Helsinki, Finland

INTRODUCTION

Stable neutral clusters (approximately 1.0 nm in diameter) have been proposed to exist in the atmosphere (e.g. Kulmala *et al.*, 2000; Kulmala *et al.*, 2005) and play an important role in new particle formation processes via their activation (Kulmala *et al.*, 2006a). Proper candidates for these clusters have been suggested to be, for instance, ammonium bisulphate clusters and their multimers (e.g. Kim *et al.,* 1998; Vehkamäki *et al.*, 2004). However, the presence of neutral atmospheric clusters has not been experimentally verified so far, since the current commercially available instruments typically cannot detect particles smaller than 3 nm.

Ion clusters even smaller than 1 nm, on the other hand, can be detected with current instruments, such as Air Ion Spectrometer (AIS) and Balanced Scanning Mobility Analyzer (BSMA). Ion clusters have been proven to exist in the atmosphere at several different locations practically all the time (see e.g. Hõrrak *et al.*, 1998). The number concentrations of these cluster ions, however, are typically so low that they cannot alone explain the observed new particle formation events (see e.g. Laakso *et al.*, 2006).

Recently significant effort has been made to develop instruments that measure neutral particles smaller than 3 nm. In this study we use two such instruments, NAIS (Neutral Air Ion Spectrometer) and UF-02proto CPC (see Mordas *et al.,* 2005). NAIS is similar to AIS, but the aerosol sample is charged with a corona charger before the electrical detection. UF-02proto, on the other hand, is a novel condensation particle counter, which, according to recent calibrations, has the potential to detect particles as small as 1.8 nm.

The composition and therefore the activation properties of the fershly formed and growing nucleation mode can be investigated using Condensation Particle Counter Battery (CPCB, see Kulmala *et al.,* 2006a). The instrument consists of four CPCs, two with butanol (TSI3010 and TSI3025) and two with water (TSI3785 and TSI3786) used as the working fluid. Therefore, in the case of highly water-soluble particles, the water CPCs detect them at smaller sizes (even below 3 nm) than the instruments based on butanol. An opposite effect is of course expected for particles that are soluble rather in butanol than water.

Our aim in this work is to detect neutral atmospheric particles smaller than 3 nm with NAIS and UF02-proto CPC pair. We also compare the measured data firstly with the corresponding ion concentrations obtained with BSMA and AIS, and secondly with theoretical predictions presented by Kerminen and Kulmala (2002). The composition of the freshly nucleated particles is studied with CPCB.

MATERIALS AND METHODS

All the data studied in this work has been measured in Hyytiälä, southern Finland, during spring 2006. For a detailed analysis, we picked four new particle formation events, taking place 22.-25.4.2006. On these days, measured particle concentrations are available for both NAIS and the UF-02proto CPCs, as well as for AIS, BSMA and CPCB. The ambient particle concentrations between 1.8 and 3.0 nm measured by NAIS were compared with the concentrations measured with a pair of UF-02proto CPCs. The cut-off sizes of these CPCs were calibrated to 1.8 and 3.0 nm (see Sipilä *et al.*, 2006) to obtain the total 1.8 – 3.0 nm particle concentration. The measured concentrations were further compared with the corresponding ion concentrations obtained by BSMA and AIS.

Theoretical predictions for 1.8 – 3.0 nm particle concentrations were calculated with a formula presented by Kerminen and Kulmala (2002) and compared with the measured data. The formula is very sensitive to the growth rate of 1-3 nm particles, which is extremely difficult to determine exactly. It is therefore noted that these predictions should be treated as order of magnitude estimations only.

RESULTS AND DISCUSSION

The total number concentrations of particles between 1.8 and 3.0 nm measured by the NAIS and UF-02proto CPC pair on an exemplary day (23.4.2006) are presented in the upper panel of Figure 1. Corresponding total ion concentrations are presented in the lower panel. The concentrations measured by the instruments including neutral particles are typically in the order of several thousands /cm^3, whereas typical ion concentrations are some tens or hundreds of particles

/cm^3. Theoretical calculations predict concentrations ranging from the order of 1000 / cm^3 to 100 000 /cm^3.

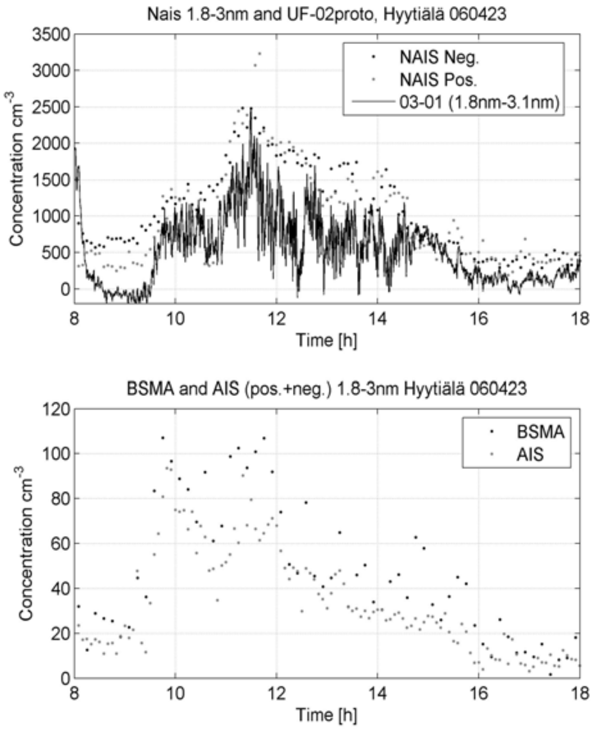

Figure 1. The 1.8-3.0 nm particle number concentrations on 23.4.2006 measured by NAIS and UF-02proto CPC pair (upper panel) and the ion instruments BSMA and AIS (lower panel). Theoretical calculations predict particle number concentrations of approximately 4000 /cm^3 at 12:00.

During new particle formation events, the CPCB practically always detects water soluble particles in the growing nucleation mode: in the beginning of the event the concentrations detected by water CPCs rise before the corresponding increase is seen with the butanol CPCs. During the event the ultrafine water CPC (3 nm cut size for silver particles) typically detects 10-20 % more particles compared to the ultrafine butanol CPC, whereas the corresponding fraction for the CPCs with the 10 nm cut size instruments are usually in the order of 50-100 %.

CONCLUSIONS

It is promising that consistent 1.8 – 3.0 nm particle concentrations can be observed with both NAIS and the UF-02proto CPC pair. The concentrations are also consistent with the corresponding ion measurements, being 10-100 times higher than the observed ion concentrations during a new particle formation event. Theoretical calculations on the particle concentrations give similar results as observed experimentally. Detailed calibrations of NAIS, however, are currently in progress and will give us further confirmation about the accuracy of the measurements.

CPCB measurements suggest that during new particle formation events, the nucleation mode particles in Hyytiälä consist of water soluble particles. This is in agreement with the strong correlation that new particle formation has with e.g. observed sulphuric acid concentrations (see e.g. Sihto *et al.*, 2006).

Keywords: *New Particle Formation, Neutral clusters*

REFERENCES

Hõrrak, U., Salm, J. and Tammet, H. (1998). Bursts of intermediate ions in atmospheric air, *J. Geophys. Res.*, 103, 13909-13915.

Kerminen, V.-M. and Kulmala, M. (2002). Analytical formulae connecting the ”real” and “apparent” nucleation rate and the nuclei number concentration for atmopheric nucleation events, *J. Aerosol Sci.*, 33, 609-622.

Kim, T.O. *et al.* (1998). Nanometer-sized particle formation from $NH_3/SO_2/H_2O$/Air mixtures by ionizing irradiation. *Aerosol Sci. Technol.*, 29, 111-125.

Kulmala, M. *et al.* (2005). On the existence of neutral atmospheric clusters, *Bor. Env. Res.*, 10, 79-87.

Kulmala, M., Lehtinen, K.E.J. and Laaksonen, A. (2006a). Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulphuric acid concentration, *Atmos. Chem. Phys.*, 6, 787–793.

Kulmala, M. *et al.* (2006b). The condensation particle counter battery (CPCB): A new tool to investigate the activation properties of nanoparticles, *submitted to J. Aerosol Sci*.

Kulmala, M., Pirjola, L. and Mäkelä, J. M. (2000). Stable sulphate clusters as a source of new atmospheric particles, *Nature*, 404: 66-69.

Laakso, L. *et al.* (2006), Contribution of ion-induced nucleation on tropospheric nucleation, *These proceedings*.

Mordas, G. *et al.* (2005). Design and performance characteristics of a condensation particle counter UF-02proto, *Bor. Env. Res.*, 10, 543-552.

Sihto, S.-L. *et al.* (2006). Atmospheric sulphuric acid and aerosol formation: Implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos. Chem. Phys. Discuss.*, 6, 3845-3882.

Sipilä, M. *et al.* (2006) Measuring Aerosol Particles below 3 nm by Condensation Particle Counter UF–02proto, *These proceedings.*

Vehkamäki, H. *et al.* (2004). Stable Ammonium Bisulphate Clusters in the Atmosphere, *Phys. Rev. Letters,* 93: Art. No. 148501.

Do we know anything about the composition of coastal nanoparticles?

Gordon McFiggans[1], James Allan[1], Rachel Burgess[1], Hugh Coe[1], Michael Cubison[1,5], Russell Saunders[2], John Plane[2], Alfonso Saiz-Lopez[2,6], Carl Palmer[3], Lucy Carpenter[3], Frithof Küpper[4]
[1]Centre for Atmospheric Sciences, University of Manchester, Manchester, M60 1QD, England
[2]Department of Chemistry, University of Leeds, Leeds, LS2, England
[3]Department of Chemistry, University of York, YO10 3DD, England
[4]Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland

INTRODUCTION

Over the last decade, there has been considerable interest in the formation and growth of particles in the coastal environment, largely precipitated by observations of coastal particle bursts at the Mace Head Atmospheric Observatory on the West Coast of Ireland. Progress has been made in characterising the phenomenology of the events and in identifying the broad mechanism and precursors responsible for the particle formation. However, there remains significant disagreement about the exact precursors and mechanisms involved. A predictive framework for coastal particle formation is therefore elusive and assessment of the broader significance in terms of local aerosol burden and regional (or even global) radiative effects awaits such a framework. This paper summarises the paucity of our mechanistic understanding of coastal particle formation and identifies some of the many remaining questions.

THE ORIGIN AND NATURE OF COASTAL PARTICLE PRECURSORS

Coastal field studies have shown that particle formation occurs overwhelmingly during the daytime. Since sulphuric acid is known to readily nucleate, it was explored whether the photochemical formation rate of H_2SO_4 was sufficient to explain the observed particle formation and growth (O'Dowd et al., 1999). It was shown that, at the concentrations of OH and SO_2 measured during the East Atlantic Summer Experiment '97 (EASE'97), there would be insufficient condensable material to explain the observed particle distribution – requiring an additional precursor – though it was possible that H_2SO_4 may have been responsible for the initial nucleation. Carpenter et al. (1999) reported the correlation between tidal exposure of macroalgae and photolabile iodocarbons, including diiodomethane (CH_2I_2), measured during the same field experiment. Alicke et al. (1999) and Allan et al. (2000) reported measurements of photochemically produced reactive iodine monoxide from the same experiment, leading to the investigation of the impacts of iodine photochemistry around daytime low tide reported in McFiggans et al. (2000) – and to a postulated involvement of iodine in particle formation through photochemically produced hydroiodic acid (HI) (A. Laaksonen, University of Helsinki, pers. comm., Jan 1998). Allan et al. (2001) reported the measurements of iodine dioxide (OIO). Further extensive field measurements during the Particle Formation in the Coastal Environment experiment (PARFORCE, O'Dowd et al., 2002) reinforced the daytime low tide relationship and led to the postulation that the particles comprised a significant amount of condensable material formed from the dimerisation of OIO photochemically formed from CH_2I_2 released by macroalgae (Hoffmann et al, 2001); the resulting particles assumed to comprise I_2O_4. This was developed by Jimenez et al. (2002) and O'Dowd et al. (2002) in aerosol chamber studies using CH_2I_2 as a precursor and coupled to a model based on that of McFiggans et al. (2000). A laboratory study of the iodine system was used to develop a model of particle formation assuming formation by OIO dimerisation (Burkholder et al, 2004). However, an alternative model predicated on findings from *ab initio* molecular dynamics calculations of the stability of higher iodine oxides was able to simulate size distributions measured in preliminary flow reactor studies and was presented by McFiggans (2002).

During the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) field project at Mace Head in 2002, molecular iodine (I_2) was measured in the atmosphere for the first time (Saiz-Lopez & Plane, 2004). Since any photochemically-produced iodine-containing particle precursor must initially be formed from atomic iodine reacting with ozone, the measured I_2 and CH_2I_2 concentrations were used along with spectrally-resolved actinic flux measurements to calculate atomic iodine production rate from each parent species (McFiggans et al., 2004). It was shown that the potential to form condensable precursors from I_2 was around 3 orders of magnitude higher than from CH_2I_2. McFiggans et al. (2004) also reported the results of ozone exposure studies of *Laminaria digitata* macroalgae carried out during NAMBLEX and more extensive flow reactor studies using *L. digitata* or I_2. It was shown that the particles formed in both cases were identical in composition to those formed in the Jimenez et al. (2002) and O'Dowd et al. (2002) studies (AMS fragmentation patterns were consistent with iodine oxides and oxy-acids – with no discernable sulphate fragments). If any condensable precursor is formed from CH_2I_2 photooxidation, it is therefore likely that around a thousand times as much originates from available I_2 and it would not be possible to discriminate between any particles formed. This was clarified in McFiggans (2005), where it was also stated that, if iodine is to play a role in particle formation in the remote ocean, there must be an abundance of undiscovered photolabile iodine. Allan et al. (2000) measured significant reactive iodine in remote oceanic air; so such a source is not unlikely.

Saiz-Lopez et al. (2006) used a simple coupled model of photochemistry and aerosol microphysics to interpret measurements made during NAMBLEX and were able to reproduce observed particle bursts using measured I_2 concentrations as the iodine source. This modelling approach required participation of the IO cross-reaction product I_2O_2 as a stable condensable species. In addition, many intermediate products need to be assumed and rate expressions estimated, since they are not currently accessible to identification and measurement. It does not require that H_2SO_4 is the initial nucleating species. This modelling approach predicts that the particles make an appreciable contribution to the background aerosol concentration some distance inland under onshore winds.

There is evidence that the particles formed in the flow reactor studies reported in McFiggans et al. (2004) were quite aspherical in nature (TEM analyses), becoming more-so as they were (artificially) grown to sizes greater than observed in the atmosphere (HTDMA reducing GF_D with increasing size but identical composition). Saunders and Plane (2006) have developed an approach based on further flow reactor studies to consider the fractal growth of the particles which is better able to replicate the laboratory observations. In all the flow reactor studies the particle stoichiometry is similar to I_4O_9 or I_2O_5.

Palmer et al. (2006) reported results from *L. digitata* exposure studies, showing tentative increases in the concentration of particles formed with increasing ozone consumed and molecular iodine produced. No relationship between formed iodocarbons and particles was observed – consistent with iodocarbon emissions being unimportant with respect to particle formation. There is strong evidence that ozone is required for I_2 release, not only for the iodine photochemistry.

NEXT STEPS & OPEN QUESTIONS

There are a number of unanswered questions of importance beyond physico-chemical curiosity.

For coastal particles to efficiently act as CCN, they must significantly add to the pre-existing number population. In order to establish whether the number of viable particles added to the coastal atmosphere is solely determined by condensable iodine, it is necessary to establish whether the precursor molecule will cluster more efficiently at atmospheric levels than available competitor species (e.g. H_2SO_4). Even if the formation of viable particles requires a "stable" nucleus, the ability to grow the nucleus to viable size requires knowledge of the thermodynamic properties. One must unambiguously determine the precursor oxides before we can understand the formation mechanism in a predictable manner. Such identification will be difficult, but for the highly polar higher oxides, microwave spectroscopy could prove useful.

Much additional useful information can be obtained from further field and laboratory / mesocosm studies. The flux response of the dominant parent molecule, I_2, on exposure of various macroalgal species to atmospheric and aqueous oxidant during daytime low tide is unknown. In the ongoing (ending 1st October 2006) RHaMBLe experiment in Roscoff in the North of France, we are measuring I_2 and iodocarbon fluxes by REA, ufp and O_3 fluxes by EC, I_2, iodocarbon, IO, OIO, O_3 and NO_x concentrations by an array of optical and mass spectrometric techniques. We shall have some further insights into these questions soon!

CONCLUSIONS

Understanding coastal particle formation requires an understanding of the interactions between the macroalgal biochemistry, aqueous redox chemistry, gas phase photochemistry and aerosol microphysics. Interpretation of field measurements requires knowledge of the macroalgal distribution and exposure through the tidal cycle and micrometeorological influences between emission and measurement.

Keywords: *Coastal particles, Aerosol formation, Composition, Laminaria, Iodine*

REFERENCES

Alicke B., Hebestreit, K., Stutz, J. & Platt, U. (1999). *Iodine oxide in the marine boundary layer*. *Nature*, 397, 6720, 572-573.

Allan. B. J., McFiggans, G., Plane, J. M. C. & Coe, H. (2000). *Observations of iodine monoxide in the remote marine boundary layer*, *J. Geophys. Res.*, 105, 14361-14369.

Allan. B. J., Plane J. M. C. & McFiggans, G. (2001). *Observations of OIO in the remote marine boundary layer*, *Geophys. Res. Letts.*, 28, 1945-1948.

Burkholder, J. B., Curtius, J., Ravishankara, A. R., & Lovejoy, E. (2004). *Laboratory studies of the homogeneous nucleation of iodine oxides*, *Atmos. Chem. Phys.*, 4, 19-34.

Carpenter, L. J., Sturges, W. T., Penkett, S. A., Liss, P. S., Alicke, B., Heibestreit, K. & Platt, U. (1999). *Short-lived alkyl iodides and bromides at Mace Head, Ireland: links to biogenic sources and* *halogen oxide production*, *J. Geophys. Res.*, 104, 1679-1689.

Hoffmann, T., O'Dowd, C. D., & Seinfeld, J. H. (2001). *Iodine oxide homogeneous nucleation: An explanation for coastal new particle production, Geophys. Res. Lett.*, 28, 1949–1952.

Jimenez, J. L., Bahreini, R., Cocker, D. R., Zhuang, H., Varutbangkul, V., Seinfeld, R. C., O'Dowd, C. D., & Hoffmann, T. (2003). *New particle formation from photooxidation of diiodomethane (CH_2I_2), J. Geophys. Res.-Atmos*, 108, 4318, doi:4310.1029/2002JD002 452, 2003.

McFiggans, G. (2005), *Marine aerosols and iodine emissions, Nature*, 433, 7026, 2005.

McFiggans, G., Plane, J. M. C., Allan, B. J., Carpenter, L. J., Coe, H., & O'Dowd, C. (2000). *A modeling study of iodine chemistry in the marine boundary layer, J. Geophys. Res.-Atmos*, 105, 14 371–14 385.

McFiggans, G. (2002). *Modelling the formation of aerosol due to iodine photochemistry – from the laboratory to the atmosphere?*, Proceedings of the CERC 3 Young Chemists Workshop - Atmospheric Chemistry and Particulate Matter, Magleås, University of Copenhagen, Denmark, 3rd-6th June.

McFiggans, G., Coe, H., Burgess, R., Allan, J., Cubison, M., Alfarra, M. R., Saunders, R., Saiz-Lopez, A., Plane, J. M. C., Wevill, D. J., Carpenter, L. J., Rickard, A. R., & Monks, P. S. (2004). *Direct evidence for coastal iodine particles from Laminaria macroalgae – linkage to emissions of molecular iodine, Atmos. Chem. Phys.*, 4, 701–713.

O'Dowd, C., McFiggans, G., Creasey, D. J. et al. (1999). *On the photochemical production of new particles in the coastal boundary layer, Geophys. Res. Lett.*, 26, 1707–1710.

O'Dowd, C. D., Hämeri, K., Mäkelä, J. M., et al. (2002). *A dedicated study of new particle formation and fate in the coastal environment (PARFORCE): Overview of objectives and achievements, J. Geophys. Res.*, 107, D19, 8108.

O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hämeri, K., Pirjola, L., Kulmala, M., Jennings, S. G., & Hoffmann, T. (2002) *Marine aerosol formation from biogenic iodine emissions, Nature*, 417, 632–636.

Palmer, C. J., Anders, T. L., Carpenter, L. J., Küpper, F. C. & McFiggans, G. (2005). *Iodine and halocarbon response of Laminaria digitata to oxidative stress and links to atmospheric new particle production, Environmental Chemistry*, 2 282-290.

Saiz-Lopez, A. and Plane, J. M. C. (2004). *Novel iodine chemistry in the marine boundary layer, Geophys. Res. Lett.*, 31, L04112, doi:04110.01029/02003GL019215

Saiz-Lopez, A., Plane, J. M. C., McFiggans, G., Williams, P. I., Ball, S. M., Bitter, M., Jones, R. L., Hongwei, C. & Hoffmann, T. (2006). *Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation, Atmos. Chem. Phys.*, 6, 883-895.

Saunders, R. & Plane J. M. C. (2006). *Modelling the fractal formation of I_2O_5 nanoparticles, submitted to J. Aerosol Sci.*

Precise Mobility Measurements and their Relevance in Atmospheric Nucleation Studies

Juan Fernández de la Mora
Department of Mechanical Engineering, Yale University,PO Box 208286, New Haven, CT 05420-8286, USA

INTRODUCTION

Monitoring the early stages of nucleation in the atmosphere requires instruments able to analyze small particles, down to their molecular precursors. For ion-induced nucleation, analysis of pre-existing ions and observation of their shift towards larger sizes at the onset of nucleation can presently be carried out at high resolution with special Differential Mobility Analyzers (DMAs). Use of such DMAs with heated wire sources of metal nanoparticles (such as those described by Peineke et al., 2006) shows abundant ions formed at the wire at filament temperatures too low for particles to form. This is followed at higher temperatures by conversion of these ions into increasingly large particles (M.B. Attoui, private communication, 2006). Some of these DMAs also run up to sonic speeds (Martinez-Lozano and Fernández de la Mora, 2006), where adiabatic acceleration provides substantial cooling, and the possibility to operate the DMA under supersaturated conditions. This is similar to high speed wind tunnel tools used for homogeneous nucleation studies, with the added possibility to measure the mobility of a primary ion as it solvates at increasing supersaturation, not only below the saturated state (Makela et al. 1996), but even above it, up to the critical size. Indeed, the mobility (hence size) of the solvated cluster can be followed in the DMA as a continuous function of supersaturation, up to the critical point, where it is expected to decrease discontinuously. In the case of homogeneous nucleation, analysis of pre-existing volatiles and associated growing clusters may be carried out with a DMA or by mass spectrometry (MS), but this requires a prior stage of charging. A number of groups have analyzed atmospheric volatiles by proton transfer reactions of the intact vapor species followed by MS, showing that the process can be used in principle to monitor the whole nucleation process. These specialized mass spectrometers are not readily taken to the field, and have a limited mass range that would make it challenging to probe beyond the very early stages of nucleation. However, the relatively efficient vapor charging schemes already demonstrated with MS instruments can be used in DMA studies, with portable instruments covering a much wider range of sizes.

We have over recent years worked on the development of several tools for the analysis by electrical mobility of both, pre-existing gas phase ions, and vapor species. This work will be distilled in the presentation from the point of view of its usefulness for nucleation studies in the atmosphere. We will first describe the special features of our high resolution DMAs for small ion work, including procedures for precise mobility measurement. Also recent work enabling high-resolution mobility determination over the full 1-100 nm size range, as well as permitting sample flows as large as 100 L/min. Atmospheric studies with these DMAs would greatly benefit from the development of single particle detectors of the CNC type, which Gamero et al. (2000) have shown can detect individual arbitrarily small charged particles. Neutral nanometer particles are much harder to activate, though Magnusson et al. suggest that use of high surface tension liquids such as water and glycerol would enable activating particles slightly larger than 1 nm. The promise of water, however is limited due to its poor performance with hydrophobic particles (Liu et al. 2006), so much remains to be learned in this area.

THE DMA AS A TOOL FOR ION ANALYSIS

The resolving power of DMAs has long been known to be limited at small sizes by Brownian motion. This difficulty can be reduced by making the DMA short down to an optimal length (Rosell et al, 1996), though at the expense of limiting the ability to analyze large particles (range reduction). It can also be controlled by increasing the Reynolds number Re of the sheath gas flow. Although this possibility is restricted by the eventual appearance of turbulence, it is nonetheless possible (Fernandez de la Mora, 2002) to maintain the flow laminar at Re as high as 60,000. This has resulted in resolving powers in excess of 100 based on the inverse of the full peak width at half maximum (FWHM) (Martinez-Lozano et al. 2006). This performance is as good as that of the best conventional ion mobility spectrometers (IMS), with the added advantage associated to the much higher sensitivity associated to the steady operation of DMAs (vs., the pulsed operation of IMS systems), and to the relatively high sample flow rates available (many tens of L/min). Several practical difficulties have delayed the use of such DMAs in atmospheric studies. One is the need to use unconventionally large sheath gas flow rates (~500-2000 L/min), which can be resolved with inexpensive vacuum cleaner motors. Another difficulty has been the fact that, in order to minimize loses of highly mobile particles, high Re DMAs have operated with the outer electrode at high voltage. This feature is not only very dangerous to the operator, but precludes also the study of atmospheric ions (not of neutral particles or vapors charged at the DMA entry). One solution has been based on so-called isopotential DMAs (Martínez-Lozano, Labowsky and Fernández de la Mora, 2006). A more conventional solution involving leaky insulating tubes at the outlet has been recently implemented in a new DMA, nicknamed the Attoui DMA, sketched in figure 1. It has similar features as other shorter high Re DMAs covering a narrower size range (typically 1-15 nm), including axial entry of the sheath gas, two laminarization screens, and a convergent trumpet. This device, however has a much wider cross section, and has the additional interest of covering with uniform resolution the full size range from 1 to 100 nm (FWHM = 4.6% at 1 nm), as well as accepting sample flow rates of 100 lit/min

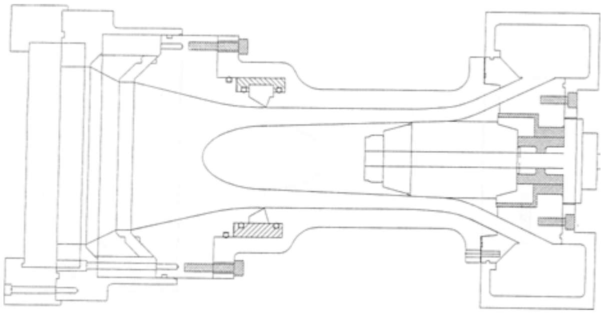

Figure 1. Sketch of the Attoui DMA

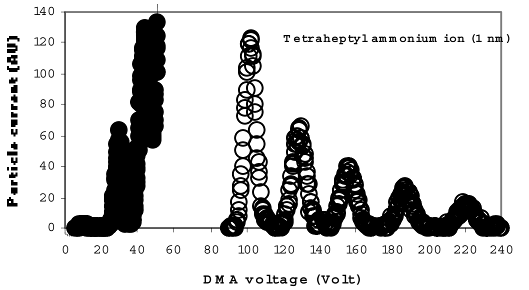

Figure 2. Performance of the Attoui DMA with monomobile ions. Open symbols are for Heptyl$_4$N$^+$ (electrical mobility Z = 0.95 cm^2/V/s; diameter ~ 1 nm), each peak corresponding to a different sheath gas flow rate Q, from 990 to 2160 L/min. The rightmost peak exhibits a full width at half height of 4.6%. Filled symbols show the spectrum of electrosprayed tetraheptyl ammonium bromide at Q = 290 Lit/min.

Another practical problem when DMAs are used at such high flow rates is the difficulty to determine accurately the flow rate (hence the mobility or the size). This obstacle can however be resolved by use of mobility standards generated by electrospray (Ude et al, 2006), whereby the precision of the mobility determination is as good as that of the standard, which may be much higher than can be attained by conventional DMA measurements.

Keywords: *nanoDMA, high flow rate, high resolution.*

REFERENCES

Fernandez de la Mora, J., (2002). Diffusion broadening in converging differential mobility analyzers, J. Aerosol Sci., **33**, 411-437

Gamero-Castaño, M. and Fernandez de la Mora, A condensation nucleus counter (CNC) sensitive to singly charged subnanometer particles; J. Aerosol Sci., **31**, 757-772 (2000).

Liu W., Kaufman S.L., Osmondson B.L., Sem G.J., Quant F.R., Oberreit D.R. (2006). Water-based condensation particle counters for environmental monitoring of ultrafine particles, J. Air & Waste Management Assoc. 56, 444-455

Magnusson, L.E., Koropchak, J.A., Anisimov, M.P., Poznjakovskiy, V. M., Fernandez de la Mora, J. (2003). Correlations for vapor nucleating critical embryo parameters, J. Phys. Chem. Ref. Data, **32**, 1387-1409

Makela JM, Riihela M, Ukkonen A, Jokinen V, Keskinen J. (1996). Comparison of mobility equivalent diameter with Kelvin-Thomson diameter using ion mobility data, J. Chem. Phys, 105 (4): 1562-1571

Martínez-Lozano, P., and Fernández de la Mora, J. (2006). Resolution improvements of a nano-DMA operating transonically, Journal of Aerosol Science, 37, 500-512

Martínez-Lozano, P., Labowsky, M., Fernández de la Mora, J. (2006). Experimental tests of a nano-DMA with no voltage change between aerosol inlet and outlet slits, J. Aerosol Science, published in the web 2/April 2006 #AS3985).

Peineke, C., Attoui, M.B., Schmidt-Ott, A. (2006), Using a glowing wire generator for production of charged,uniformly sized nanoparticles at high concentrations, J. Aerosol Sci., in press

Rosell, J., Loscertales, I. G., Bingham, D. and Fernández de la Mora, J. (1996). Sizing nanoparticles and ions with a short differential mobility analyzer", J. Aerosol Sci., **27**, 695-719.

Stolzenburg, M. R. and McMurry, P. H. (1991) An ultrfine aerosol condensation nucleus counter. *Aerosol Sci.Technol.* 14, 48-65

Ude, S., and Fernández de la Mora, J. (2006). Molecular monodisperse mobility and mass standards from Electrosprays of tetra-alkyl ammonium halides, J. Aerosol Sci, **36**, 1224-1237

About the studies of new particle formation and growth using air ion spectrometers

M. Vana[1,2], E. Tamm[2], U. Hõrrak[1,2], A. Mirme[2], H. Tammet[2], A. Hirsikko[1], L. Laakso[1] and M. Kulmala[1]
[1] *Department of Physical Sciences, Division of Atmospheric Sciences, University of Helsinki, FI-00014, Helsinki, Finland*
[2] *Institute of Environmental Physics, University of Tartu, EE-50090, Tartu, Estonia*

INTRODUCTION

Current studies of nucleation mechanisms of atmospheric aerosol particles demand the measurements of particles with diameters < 3 nm. Common aerosol spectrometers are able to measure particles with sizes > 3 nm. Air ion spectrometers designed at the University of Tartu are able to detect recently nucleated charged aerosol particles and charged clusters < 3 nm.

Simultaneous measurements of particles by ion spectrometers and aerosol spectrometers enable to give valuable information about nucleation and growth properties, and charging state of atmospheric aerosol particles. By now, we have a lot of data of air ion mobility distributions from many places around the world from Finnish Lapland to Antarctica and Australia. These measurements have given new interesting results and new data are coming every day.

APPARATUS

There are two kinds of mobility spectrometers, designed at the University of Tartu, Estonia, and built by Airel Ltd.: the Balanced Scanning Mobility Analyser (BSMA) and the Air Ion Spectrometer (AIS) measuring air ion mobility distribution. BSMA (Tammet, 2004) measures ion number concentrations in the 16 fractions consecutively in time, one polarity after the other in mobility range 3.2 – 0.032 $cm^2V^{-1}s^{-1}$ (corresponding diameter range is 0.34 nm – 7.4 nm). AIS (Mirme, 2004) measures simultaneously ion concentrations in 28 mobility fractions of both, positive and negative ions in mobility range 3.2 – 0.00075 $cm^2/V\cdot s$ (0.34 – 40 nm). The Neutral Air Ion Spectrometer (NAIS) is developed. The NAIS is able to measure also neutral particles below 3 nm. This is a modification of the AIS with added extra chargers and filters.

At present time, there are 7 AISs and two BSMAs in the world. Figure 1 shows the measurement locations and expedition routes, where these instruments have measured.

RESULTS

Some of the results obtained from the measurements are as follows:

- New particle formation and growth events have been found all over the world, except during expedition over the Atlantic ocean.

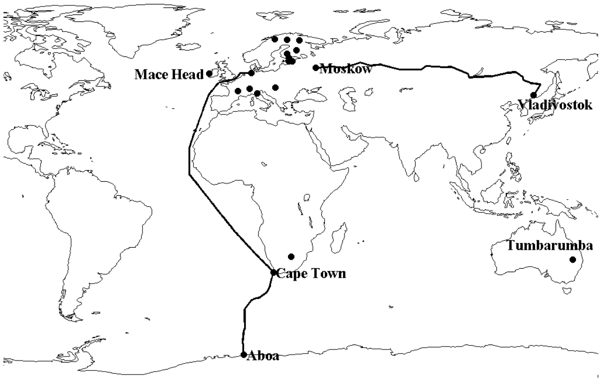

Figure 1. Locations and expedition routes of the measurements of air ion mobility distributions.

- In some cases, charged fraction as a function of size shows overcharging of 3 – 5 nm particles in relation to steady charging state, which is an indication of ion-induced nucleation.
- By comparison of AIS and NAIS data, the amount of neutral 1 – 3 nm particles is estimated.
- Formation of 2 – 6 nm negatively charged particles is detected during rain- and snowfall.
- Disappearance of air ions is observed during the measurements inside cloud.
- Estimated particle growth rates in the atmosphere vary between 1 – 10 nm/h in most cases. A size-dependence of growth rate is observed.
- Growth and nucleation rates obtained from measurements are compared with modelled results by Tammet's model (Tammet and Kulmala, 2005).

Keywords: *Air ions, Atmospheric nucleation, Measurement campaigns*

REFERENCES

Mirme, A. (2004) Performance of spectrometer for analysis of charged fraction of atmospheric aerosol, *J. Aerosol Sci.*, 35, S277-S278.

Tammet, H. (2006) Continuous scanning of the mobility and size distribution of charged clusters and nanometer particles in atmospheric air and the Balanced Scanning Mobility Analyzer BSMA, *Atmos. Res.*, in press.

Tammet, H. and Kulmala, M. (2005) Simulation tool for atmospheric aerosol nucleation bursts, *J. Aerosol Sci.*, 36, 173-196.

Biogenic Aerosol Formation in a Native Australian Eucalypt Forest

Tanja Suni[1], Eva van Gorsel[1], Helen Cleugh[1], Ray Leuning[1], Steve Zegelin[1], Dale Hughes[1], Mark Kitchen[1], Richard Hurley[1], Larisa Sogacheva[2], Lauri Laakso[2], Anne Hirsikko[2], Miikka dal Maso[2], Timo Vesala[2], and Markku Kulmala[2]

[1]CSIRO Marine and Atmospheric Research, GPO Box 1666, Canberra ACT 2601, Australia
[2]Division of Atmospheric Sciences, PO Box 64, FIN-00014 University of Helsinki, Finland

INTRODUCTION

The influence of aerosols on climate is the largest uncertainty in current climate models. Aerosols are produced by human activity but they are also formed naturally in oceans, deserts, and forests. Determining the magnitude and driving factors of biogenic aerosol production in different ecosystems is crucial for future development of climate models.

So far, most studies of biogenic aerosol production have taken place at continental and coastal sites in the Northern Hemisphere (Kulmala *et al.*, 2004). Our project is the first to study aerosol production rates in a temperate forest in the Southern Hemisphere. The study site is an evergreen Eucalypt forest in Tumbarumba, NSW, Australia. Our aim is to determine the magnitude of aerosol production and to find driving environmental factors in Tumbarumba and to compare the results to those obtained in other environments and climates. Our project is a step towards determining the contribution of forests to the global aerosol load.

METHODS

The initial steps of aerosol formation can be detected with a new Atmospheric Ion Spectrometer (AIS) (Laakso *et al.* 2004). The AIS we use in this project can detect charged particles (ions) down to 0.4 nm in diameter in their birth and growth phases and measures their size distribution up to about 40 nm continuously every 5 minutes.

RESULTS AND DISCUSSION

Fig. 1 shows a particle formation event that on average appears to take place every third day in Tumbarumba just like at the SMEAR II station in Hyytiälä, southern Finland. However, in Hyytiälä new particles are formed mainly in spring and autumn, but in Tumbarumba many events have taken place in the middle of winter. Suppressing factors for aerosol formation were humidity and cloudiness. RH was 58% on particle formation days (FD) and 83% on non-formation days (NFD). Similarly, cloudiness was 1.5 on FD and 3.8 on NFD. Temperature played no role, being 10 ºC on both FD and NFD. This is probably a wintertime phenomenon – high temperatures should prevent particle formation by inhibiting condensation of organic vapours. Air mass origin did not have an effect (data not shown).

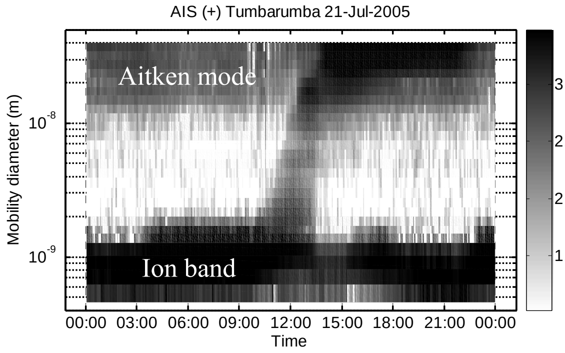

Figure 1. New particles form in Tumbarumba in July, 2005. X-axis: time (24 h), y-axis: particle diameter. Colour indicates concentration in logarithmic scale. At midday, new small particles start to grow from the ion band into the Aitken mode. From here, they can go on growing into cloud droplets.

CONCLUSIONS

First in the world, we have observed that a native Australian Eucalypt forest is at least as effective at producing new particles as the boreal forest. As expected, humidity and cloudiness appeared to suppress aerosol formation. The events were independent of air mass origin. This may mean that the statistical sample is still too small or it may indicate that the VOC emissions in the Eucalypt forest are strong enough to lead to particle formation even in the presence of pre-existing aerosol.

Keywords: *Biomass and Biogenic Aerosols, Forests, VOC and SVOC aerosols*

REFERENCES

Kulmala, M., Vehkamäki, H., Petäjä, T., *et al.*, (2004) Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J Aerosol Sci* 35, 143-176.

Laakso, L., Anttila, T., Lehtinen, K., Aalto, P., Kulmala, M., Horrak, U., Paatero, J., Hanke, M., and Arnold, F. (2004) Kinetic nucleation and ions in boreal forest particle formation events, Atmos. Chem. Phys., 4, 2353–2366.

This work was supported by the Academy of Finland, Maj and Tor Nessling Foundation, and the Centennial Foundation of Helsingin Sanomat.

Experimental Systems for Investigation of Ion-Induced Nucleation

M. Adachi and N. Yokoyama
Department of Chemical Engineering, Osaka Prefecture University, 599-8531, 1-1 Gakuen-cho Sakai Osaka, Japan

INTRODUCTION

An ion-induced nucleation is one of important mechanisms to generate an atmospheric aerosol. However, the growth from ion to particles has no been measured directly and credible growth rates of ions have not been obtained. In this paper, two experimental systems using a small ionization chamber and a differential mobility analyzer (DMA) as a nucleation chamber are reported.

ION-INDUCED NUCLEATION IN SAMLL α-RAY IONIZATION CHAMBER (T.O. Kim et al., 1997)

Figure 1 shows the experimental apparatus used consists of a continuous flow gas-generation system, an α-ray ionisation chamber, an ultarfine aerosol condensation nucleus counter (UCNC; TSI model 3025), a cluster-differential mobility analyser combined with Faraday cup electrometer (C-DMA/FCE) set.

In the ionization chamber, nanometer sized particles are generated from SO_2/H_2O/Air mixture. for ion-induced nucleation. The upper and lower walls of the chamber act as electrodes, and a ^{241} Am source of 3.03 MBq is placed on the lower wall. Then the mixture is ionized by α-ray emitted from the ^{241} Am source. By removing charged particles to one of the electrodes, the dc electric field applied to the ionisation chamber prevents charged particles from being neutralized by bipolar ions. The tungsten wire of the exit tube acts as a charged-particle collector. Particles pass through the collector are measured with the UCNC. The dc voltage is applied to the collector and the ionisation chamber when the number concentration of uncharged particles n_0 is measured. When total particles number concentration n_T is measured, the voltage is not applied to the ionizer and the collector. Then, the charged-particle fraction f=1- n_0/ n_T is given. When particle size is measured with C-DMA/FCD set, no voltage is applied to them.

Figure 2 shows electrical mobility distributions measured at SO_2 concentration of 0.3-3.3 ppm. Nano-particles are generated and their peak height increases with SO_2 concentration.

The charged-particle fraction was measured at SO_2 concentration of 0.2-1.0 ppm and the residence time of 1.46-4.39 s. The fraction decreased with increasing SO_2 concentration. The reduction of charged-particle fraction at a residence time of t_R=4.39 s was larger than those at t_R=2.20 and1.46 s.

Figure 3 shows the particle formation mechanisms clarified in this experimental system. In the SO_2/H_2O/Air mixture, particles are formed by competition between ion-induced nucleation and binary homogeneous nucleation. Hydroxyl radicals react with SO_2 and produce SO_3, which produce finally H_2SO_4 by reaction with H_2O. H_2SO_4 vapor forms particles not only by binary homogeneous nucleation with H_2O vapor but also by ion-induced nucleation. The particle formation by ion-induced nucleation is faster than that by binary homogeneous nucleation.

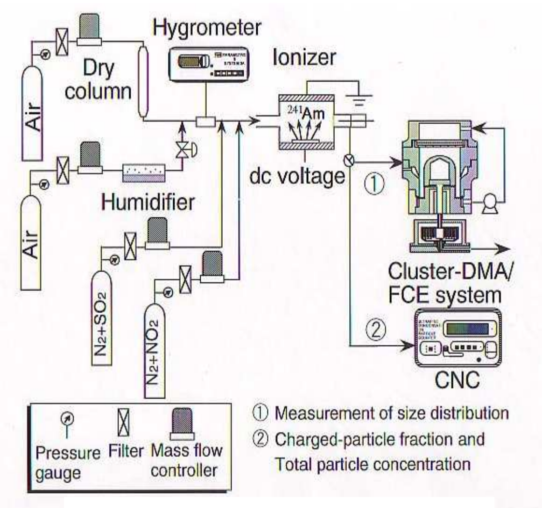

Figure 1 Experimental system using α-ray ionization chamber.

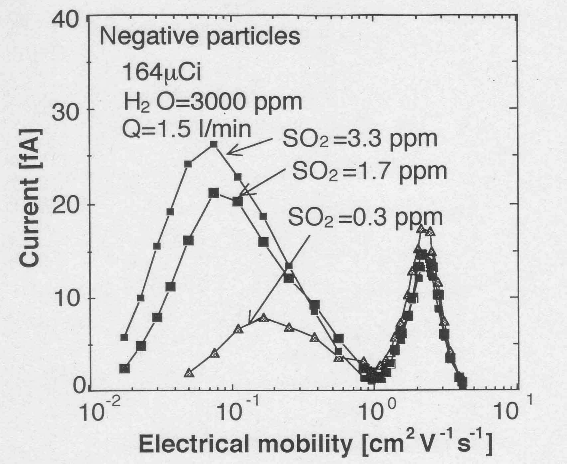

Figure 2 Change in electrical mobility distribution with SO_2 concentration.

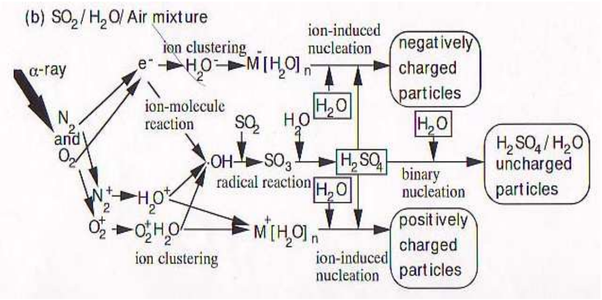

Figure 3 Particle formation mechanisms in SO_2/H_2O/Air Mixture.

ION-INDUCED NUCLEATION IN DIFFIRENTIAL MOBILITY ANALYZER (Adachi and Yokoyama, 2005)

A differential mobility analyzer (DMA) is used as a nucleation chamber (Figure 4). An air containing a condensable vapor is sent to a classification zone between outer and inner cylindrical electrodes as a sheath air. In the classification zone, ions introduced from the outer electrode are attracted to the inner electrode and cross the sheath air containing the vapor. During the crossing, vapor molecules condense on ions, that is, the ion-induced nucleation.

The experimental system consists of the Vienna type DMA/Faraday cup electrometer (FCE) set (Wyckoff Co. Model DMA Ⅲ), the evaporator, the hygrometer, the thermometer and the ion generator (Figure 5). The humidity of the sheath air is controlled. Both of the α-ray radioactive ionizer and the high-pressure ionizer are used as the ion generator. The α-ray radioactive ionizer generates the ions with standard mobility and the high-pressure ionizer dose the ions with various mobility. H_2O cluster ions and H_2SO_4/H_2O cluster ions are generated by both devises.

Figure 6 shows mobility distribution of H_2O cluster ions at humidity of 15- 28%. H_2O cluster ions were generated by the high pressure ionoizer which H_2O of 7300 ppm is added and –12kV is supplied. The peak values in the electrical mobility distributions shifted to lower values and their currents tended to be higher according to the increase in humidity in DMA. This means that H_2O cluster ions evaporate in DMA at RH=15-28%.

Keywords: *Differential mobility analyzer, Humidity, Ion-induced nucleation, Ion mobility*

REFERECCES

T.O.Kim, M.Adachi, K.Okuyama and J.H.Seinfeld (1997) Aerosol Sci. Technol., 26, 527-543.

M.Adachi and N.Yokoyama (2005) Proc. 4th Asian Aerosol Conf., p351.

This work was financially supported in part by a grant-in-aid for Developmental Scientific Research (No.16030208) from the Ministry of Education, Culture and Science of Japan.

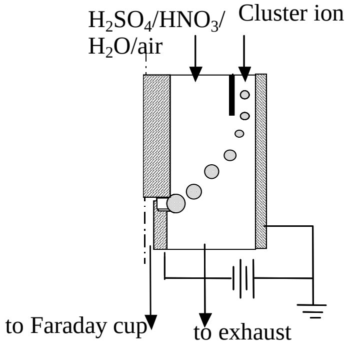

Figure 4. Ion-Induced Nucleation in DMA.

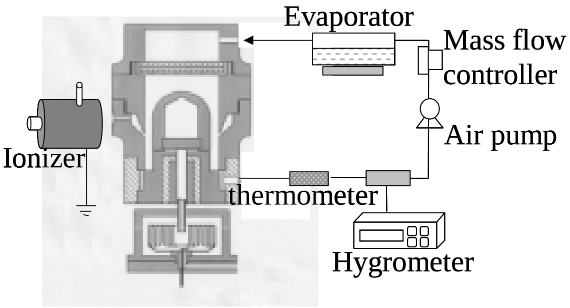

Figure 5. Experimental system

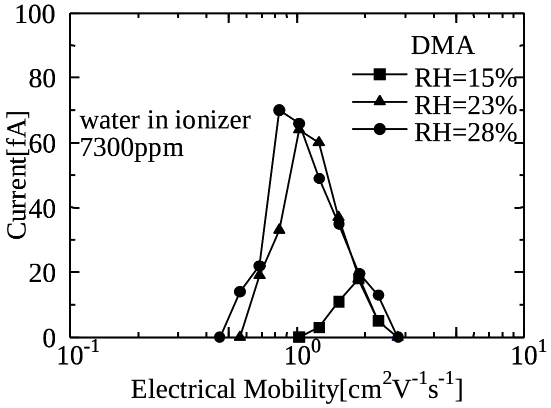

Figure 6. Electrical mobility distributions of ions at RH=15-28% in DMA.

Contributions of Organic Acids to New Particle formation

Renyi Zhang
Department of Atmospheric Sciences, Texas A&M University, College Station, TX 77843, USA

INTRODUCTION

To assess the role of low volatile organic species in new particle formation, we perform laboratory studies of particle nucleation from several acid vapors and their mixtures with H_2SO_4. Nucleation of sulfuric acid is considerably enhanced in the presence of organic acids. Theoretical calculations identify the formation of an unusually stable aromatic acid-sulfuric acid complex, which likely leads to a reduced nucleation barrier. In addition, we performed aerosol simulations using a chemical transport model and ground-based and aircraft aerosol measurements to investigate the contribution of low-volatility organics in new particle formation in an urban environment. The results imply that the interaction between organic and sulfuric acids promotes efficient formation of organic and sulfate aerosols.

EXPERIMENTAL STUDIES

Aerosol nucleation experiments were performed using an aerosols chamber coupled to ion drift - chemical ionization mass spectrometry (ID-CIMS) and nano-differential mobility analyzer (Nano-DMA) for gaseous and particle detection, respectively (1). We initially generated H_2SO_4 aerosols by introducing gas-phase H_2SO_4 in a nitrogen carrier gas with a variable relative humidity (RH). For a gaseous H2SO4 concentration in the range of 10^9 to 10^{10} molecule cm^{-3}, the particle size formed ranged from 3 to 10 nm. The observed particle concentration increased when the gaseous H_2SO_4 concentration or RH was increased. A marked increase in the particle concentration occurred when organic acid vapor was added to the aerosol chamber (Fig. 1).

The nucleation rate, J, was estimated on the basis of the ratio of the measured particle concentration to the nucleation time. In the absence of organic acids, the nucleation rate is dependent on the gas-phase H_2SO_4 concentration and RH. The nucleation rate was considerably increased in the presence of the organic acids (Fig. 2).

QUANTUM CHEMICAL CALCULATIONS

We performed quantum chemical calculations which show the formation of surprisingly stable aromatic acid-sulfuric acid complexes (Fig. 3). The equilibrium aromatic acid-sulfuric acid structure exhibits a nearly planar eight-membered ring: there are two hydrogen bonds with the organic acid molecule acting as both a hydrogen-bond donor and acceptor. The binding energies of the complexes are about 20 kcal mol^{-1} for most organic acids. The large stability of the organic acid-sulfuric acid complex implies that the aromatic acid molecule bonds irreversibly to H_2SO_4 under atmospheric conditions. The complex formation between aromatic and sulfuric acids most likely reduces the barrier in heteromolecular nucleation and helps condensation growth of the nucleated critical embryo by overcoming the Kelvin effect.

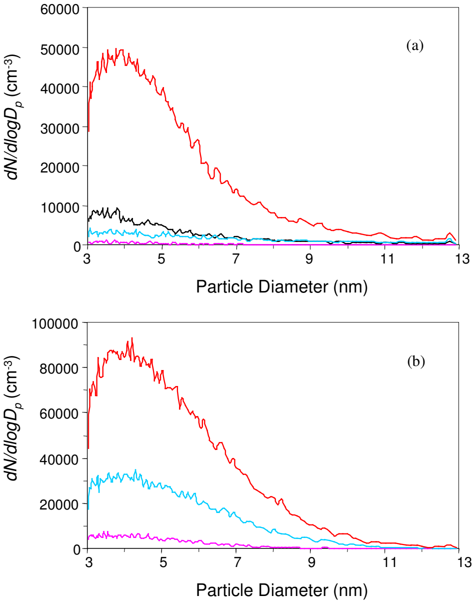

Figure 1. Measured particle size distributions of the nucleating aerosols. In (a), the pink and black curves correspond to H2SO4 aerosol formation with a RH of 5% and gaseous H2SO4 concentrations of 6 x 10^9 and 8 x 10^9 molecule cm^{-3}, respectively. The blue and red curves are similar to the pink and black curves, respectively, except for addition of 0.04 ppb benzoic acid to the aerosol chamber. In (b), the pink curve corresponds to H_2SO_4 aerosol formation with a RH of 5% and a gaseous H_2SO_4 concentration of 7 x 10^9 molecule cm^{-3}. The blue and red curves are similar to the pink curve, except for the addition of 0.04 and 0.1 ppb benzoic acid (corresponding to 1 x 10^9 and 2.5 x 10^9 molecule cm^{-3}), respectively.

MEASUREMENTS AND MODELING

In addition, we performed aerosol simulations using the EPA's Models-3 Community Multiscale Air Quality model (CMAQ) and ground-based and aircraft aerosol measurements to investigate new particle formation in an urban environment (Fig. 4). The aerosol measurements reveal elevated ultrafine particles that reach the highest value in the afternoon, indicating prominent new particle formation. Simulations of the binary H_2SO_4-H_2O nucleation predict an order of magnitude lower concentrations for aerosols near 10 nm than the measurements. A parameterized nucleation scheme that accounts for the enhanced nucleation effect of secondary condensable organics is incorporated into the Models-3/CMAQ. The organic nucleation scheme predicts the number concentrations in agreement with the ground-based and aircraft measurements during the daytime.

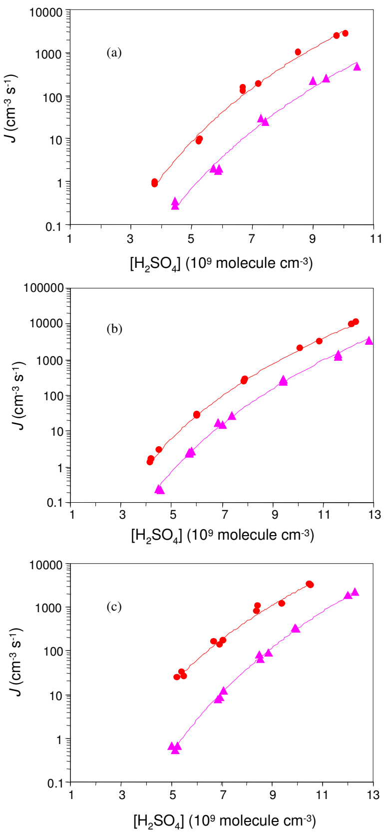

Figure 2. Measured nucleation rate (J) as a function of gaseous H_2SO_4 concentration. The solid triangles correspond to H_2SO_4 aerosol formation with a RH of 5%, and the solid circles correspond to particle formation with 5% RH and in the presence of 0.1 ppb benzoic acid (a), 0.2 ppb p-toluic acid (b), and 0.3 ppb m-toluic acid (c). The curves are fit to the experimental data. The experiments were performed at 298 ± 2 K and a total pressure of 760 Torr.

CONCLUSIONS

Our combined experimental studies, quantum chemical calculations, measurements and modeling corroborate the importance of secondary condensable organics in new particle formation when sulfate and organics are abundant.

Keywords: *Organic acids, nucleation, sulfuric acid*

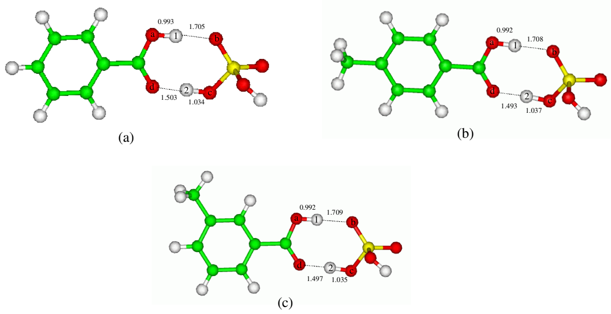

Figure 3. Equilibrium geometries of the benzoic acid (a), p-toluic acid (b), and m-toluic acid (c) - sulfuric acid complexes obtained at the B3LYP/6-31G(d,p) level of theory.

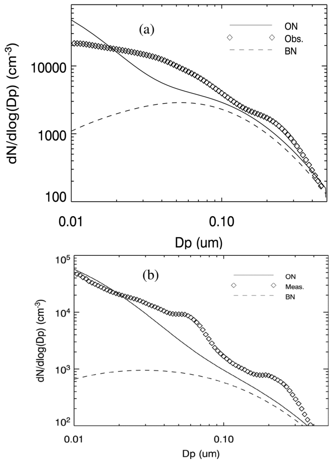

Figure 4. Comparison of aerosol simulations with the ground-level (a) and aircraft (b) measurements. The solid, dashed, and diamond curves correspond to simulations using the ON scheme and BN scheme and measurements, respectively.

REFERENCES

Fan, J., R. Zhang, D. Collins, and G. Li, Contribution of secondary condensable organics to new particle formation: A case study in Houston, Texas, Geophys. Res. Lett. 33, L15802, doi:10.1029/2006GL026295 (2006).

Zhang, R., I. Suh, J. Zhao, D. Zhang, E.C. Fortner, X. Tie, L.T. Molina, and M.J. Molina, Atmospheric new particle formation enhanced by organic acids, Science 304, 1487-1490 (2004).

This work was supported by the NSF, DOE, and Texas Air Research Center (TARC).

Measurements of Potential Aerosol Precursor Gases in the Rural and Coastal Atmosphere

H. Berresheim and C. Plass-Duelmer
German Weather Service, Meteorological Observatory, 82383 Hohenpeissenberg, Germany

INTRODUCTION

Sulfuric acid (H_2SO_4) and other potential precursor gases for ultrafine particle (UFP) formation have been measured in several field campaigns spanning from a few weeks up to several years. In collaboration with other research groups measuring aerosol physical and chemical parameters these studies have been conducted in quite different environments: (a) rural (Hohenpeissenberg, southern Bavaria, Germany; Birmili et al., 2003), and (b) coastal marine (Mace Head, Ireland; Berresheim et al., 2002; O'Dowd et al., 2003; and Finokalia, Crete/Greece; Berresheim et al., 2003; Bardouki et al., 2003).

RURAL ATMOSPHERE

From April 1998 to August 2000 the Hohenpeissenberg Aerosol Formation Experiment (HAFEX) was carried out at the Global Atmosphere Watch (GAW) Observatory Hohenpeissenberg (47°48'N, 11°01'E). H_2SO_4 and OH were measured by chemical ionization mass spectrometry (CIMS; Berresheim et al., 2000; Rohrer and Berresheim, 2006), monoterpenes and other hydrocarbons by GC/FID/MS. The long-term H_2SO_4 record (Figure 1) shows significant annual variation with maximum levels in spring and summer. Monoterpenes are strongly emitted from the forest area surrounding the observatory and, as expected, also peak in summer. On the other hand, apparent UFP (particles detectable between 3-11 nm diameter) were mostly observed during winter/spring (20% of all measurement days) and fall, but rarely and with lower number concentrations in summer (Birmili et al., 2003). UFP events only occurred around local midday hours and in most cases during high pressure and sunny conditions in subsiding air with elevated OH and H_2SO_4 levels. Overall, a classification by the intensity of the events indicated a qualitative relation between observed UFP and H_2SO_4 levels except for the summer season. However, a simple correlation between the two parameters is not evident from the measurements (Figure 2) . Photochemical H_2SO_4 production is likely important for UFP formation but apparently does not suffice to trigger a (measurable) UFP event. Maximum production rates of H_2SO_4 reach up to $2x10^5$ cm^{-3} s^{-1} , those of total monoterpene oxidation products (MOPs) contributing to UFP mass (10-20% of all products) may even be higher in summer and comparable in spring and fall. With respect to further particle growth, H_2SO_4 contribution is likely minor compared to that by MOPs. Growth rates on the order of 2 nm/hr were calculated. Further calculations indicated that the total aerosol surface concentration is a critical factor with respect to "survival and growth" (in competition with coagulation) of UFP. However, no significant seasonal variation of this parameter was found at Hohenpeissenberg.

COASTAL ATMOSPHERE

As part of the PARFORCE campaign (New Particle Formation and Fate in the Coastal Environment, June 1999) CIMS measurements at Mace Head revealed that H_2SO_4 can initiate (ternary) particle nucleation also in this type of environment, and in conjunction with iodine compounds promote the growth of 1 nm to 3 nm and larger particles (Kulmala et al., 2002; O'Dowd et al., 2004). High time resolution data showed some inverse correlations between UFP levels and both H_2SO_4 and MSA levels with the latter contributing only to particle growth. UFP events systematically occurred at low tide and showed no overall correlation with H_2SO_4. Dimethylsulfide oxidation alone (assuming only SO_2 as intermediate product) could not explain observed H_2SO_4 levels. OH measurements during UFP events pointed to a significant consumption of OH and fast photochemistry involving reactions with organic compounds released from seaweed.

During the MINOS campaign (Mediterranean Intensive Oxidant Study, July/August 2001) on the northeastern coast of Crete consistently polluted air was encountered (Lelieveld et al., 2002) and no UFP events were observed in the marine boundary layer. H_2SO_4 concentrations were balanced by formation via SO_2+OH reaction and condensation onto existing aerosol. The latter process contributed up to two thirds to aerosol non-sea salt sulfate levels. The H_2SO_4 lifetime was quite low at 1-2.5 min (Bardouki et al., 2003).

CONCLUSIONS

UFP formation in both rural and coastal background air requires photochemical processing and can be initiated by H_2SO_4. However, additional controls by aerosol surface concentration, temperature, relative humidity and/or air mass exchange may be critical. In rural air H_2SO_4 production rates can be exceeded by production of MOPs which thus contribute significantly to aerosol mass.

Keywords: *sulfuric acid, hydrocarbons, measurements, aerosol nucleation, aerosol growth*

REFERENCES

Bardouki, H., H. Berresheim, M. Vrekoussis, J. Sciare, G. Kouvarakis, K. Oikonomou, J. Schneider, and N. Mihalopoulos, Gaseous (DMS, MSA, SO_2, H_2SO_4 and DMSO) and particulate (sulfate and methanesulfonate) sulfur species over the northeastern coast of Crete, *Atmos. Chem. Phys.*, *3*, 1871-1886, 2003.

Berresheim, H., C. Plass-Dülmer, T. Elste, N. Mihalopoulos, and F. Rohrer, OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis, *Atmos. Chem. Phys. , 3*, 639-649, 2003.

Berresheim, H., T. Elste, H. G. Tremmel, A. G. Allen, H.-C. Hansson, K. Rosman, M. DalMaso, J. M. Mäkelä, M. Kulmala, and C. D. O'Dowd, Gas-aerosol relationships of H_2SO_4, MSA, and OH: Observations in the coastal marine boundary layer at Mace Head, Ireland, *J. Geophys. Res.*, *107*(D19), 8100, doi: 10.1029/2000JD000229, 2002.

Berresheim, H., T. Elste, C. Plass-Dülmer, F.L. Eisele, and D.J. Tanner, Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H_2SO_4, *Int. J. Mass Spectrom.*, *202*, 91-109, 2000.

Birmili, W., H. Berresheim, C. Plass-Dülmer, T. Elste, S. Gilge, A. Wiedensohler, and U. Uhrner, The Hohenpeissenberg aerosol formation experiment (HAFEX): A long-term study including size-resolved aerosol, H_2SO_4, OH, and monoterpene measurements, *Atmos. Chem. Phys.*, *3*, 361-376, 2003.

Lelieveld, J., H. Berresheim, S. Borrmann, P. J. Crutzen, F. J. Dentener, H. Fischer, J. de Gouw, J. Feichter, P. Flatau, J. Heland, R. Holzinger, R. Korrmann, M. Lawrence, Z. Levin, K. Markowicz, N. Mihalopoulos, A. Minikin, V. Ramanathan, M. de Reus, G. J. Roelofs, H. A. Scheeren, J. Sciare, H. Schlager, M. Schultz, P. Siegmund, B. Steil, P. Stier, M. Traub, J. Williams, and H. Ziereis, Global air pollution crossroads over the Mediterranean, *Science*, *298*, 794-799, 2002.

O'Dowd, C.D., K. Hämeri, J.M. Mäkelä, L. Pirjola, M. Kulmala, S.G. Jennings, H. Berresheim, H.-C. Hansson, G. de Leeuw, A. G. Allen, C. N. Hewitt, A. Jackson, Y. Viisanen, T. Hoffmann, A dedicated study of new particle formation and fate in the coastal environment (PARFORCE): Overview of objectives and initial achievements, *J. Geophys. Res.*, *107*(D19), 8108, doi: 10.1029/2001JD000555, 2002.

O'Dowd, C.D., J.L. Jimenez, R. Bahreini, R.C. Flagan, J.H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S.G. Jennigns, and T. Hoffmann, Marine aerosol formation from biogenic iodine emissions, *Nature*, *417*, 632-636, 2002.

Rohrer, F., and H. Berresheim, Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, *Nature*, *442*, 184-187, 2006.

This work was supported in part by Max-Planck Institute for Chemistry and German Federal Ministry of Research. We thank the GAW team at Hohenpeissenberg for ozone and aerosol data.

.

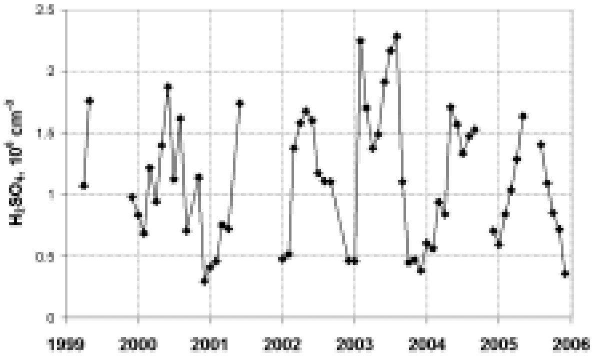

Figure 1. Atmospheric H_2SO_4 concentrations (monthly means) measured at Hohenpeissenberg (1999-2005) at ambient relative humidities <95%.

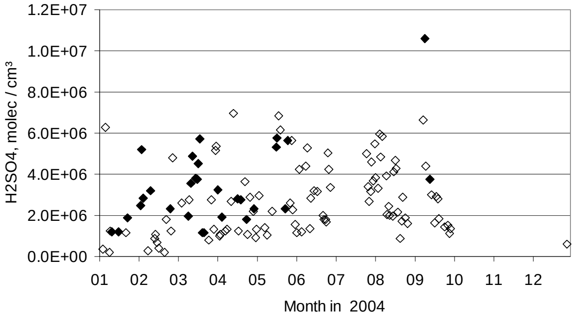

Figure 2. Atmospheric H_2SO_4 concentrations (hourly means, 1100-1400 CET) measured at Hohenpeissenberg in 2004 (ambient relative humidities <95%; filled symbols: UFP events, open symbols: all data).

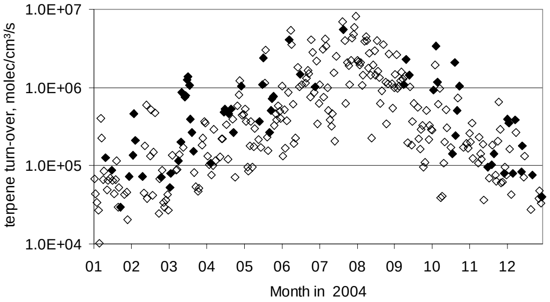

Figure 3. Total monoterpene turnover rates with OH and O_3 (hourly means, 1100-1400 CET) at Hohenpeissenberg in 2004 (filled symbols: UFP events, open symbols: all data).

The growth rate of fresh atmospheric particles: implications on vapour species and nucleation rate estimates

Miikka Dal Maso[1], Tuukka Petäjä[1], Ilona Riipinen[1], Anne Hirsikko[1], Sanna-Liisa Sihto[1], Michael Boy[1], Laura Korhonen[1], and Markku Kulmala[1]
[1]*Department of Physical Sciences, University of Helsinki, FIN-00014, Helsinki, Finland*

INTRODUCTION

During the last decade a wealth of submicron aerosol size distribution measurements has become available for scientists interested in atmospheric particle formation (see Kulmala *et al.,* 2004 for a review).

Currently, the formation of observable aerosol particles has to be considered a separate phenomenon from the actual nucleation process, as most aerosol instrumentation cannot observe particles at the sizes they are considered to be born. Between the instant of formation and the moment that particles can be observed they grow by condensation of vapour molecules, while simultaneously being scavenged by coagulation to pre-existing particles.

Among the key questions to be answered before particle formation bursts can be successfully incorporated into modelling efforts are

i) what species take part in nucleation and at which rate does it produce clusters?
ii) What condensing species is responsible for the particle growth?

Determining the rate at which the newly formed particles grow is a key factor in answering these questions; herein we will discuss some aspects of this.

METHODS AND DISCUSSION

Atmospheric, regional particle formation events are characterized by the appearance of new particles at the beginning of the spectrum and the subsequent growth of these particles. The growth rate can be determined from measured size distributions in various ways; for example, taking the time derivative of the geometric mean diameter of a suitable particle size range or a log-normal distribution fitted to the new particles (e.g. Stoltzenburg, 2005); alternatively, following the time evolution of the concentration in each measurement 'channel' (e.g Hirsikko *et al.,* 2005); or estimating the time difference of the assumed nucleation time and the time particles are observed (e.g. Fiedler *et al.,* 2005).

The observed growth rates of fresh particles range generally from ca. 0.5 nm/h to ca. 20 nm/h in different environments. The growth rate of >3 nm particles is often rather constant, but investigations of ion spectra in for example the boreal forest have shown that the early growth is slower than in the latter stages (Hirsikko *et al.,* 2005).

The theory of aerosol dynamics during a nucleation burst is well-known, and allows one to try to make a closure between the probable condensing vapour and the observed growth rate. If this is done with observations using the log-normal mode approach, one should also take into account the changes to the distribution caused by coagulation, as Stoltzenburg *et al.* (2005) have done. Comparisons of growth with measured sulphuric acid concentrations have been done, and in the very polluted environment of Atlanta good closure was achieved (Stoltzenburg *et al.,* 2005); other studies, however have shown that only a small fraction of the growth can be explained by sulphuric acid (Weber *et al.,* 1997; Fiedler *et al,* 2005; Boy *et al.,* 2005 ; Wehner *et al,* 2005).

For a longer time-series analysis, we have used modelled sulphuric acid concentrations (Boy *et al.,* 2005) with growth rates obtained from several instruments including DMPS, AIS and BSMA for events covering a time over 2 years at the Hyytiälä measuring station. The results show that the contribution of sulphuric acid varies, cannot alone explain the growth, even at the smaller sizes. This means that other, low-volatile vapours are involved in particle growth. Organic oxidation products are considered most likely candidates.

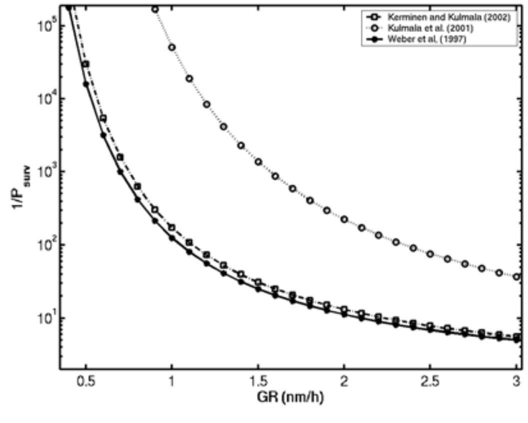

Figure 1: The factor $1/P_{surv}$ as a function of the particle growth rate for typical event conditions in Hyytiälä, Finland.

This has implications also on the determination of the nucleation rate of fresh clusters. The competition between condensation growth and coagulation loss is probably the most important process defining whether new particle formation occurs in the atmosphere. The probability of a nucleated (stable) cluster to survive to observable sizes has been studied by several authors (eg. Weber *et al.,* 1997; Kulmala *et al.,* 2001; Kerminen and Kulmala, 2002; Mcurry *et al.,* 2005). The relation between the observed formation rate can be given as

$$J_{nucleation} = \frac{1}{P_{survival}} J_{observed}$$

where $P_{survival}$ is the probability of a particle surviving the growth from nucleation size to observable size. The factor $1/P_{survival}$ depends exponentially from the growth rate; this means that at low growth rates, as they are currently assumed to be in the critical 1-3 nm range, a small difference in the growth rate can cause differences of over and order of magnitude to the obtained nucleation rate (see Fig. 1). If the growth is solely dependent on the sulphuric acid concentration, measurements of vapour phase sulphuric acid can be used for nucleation rate estimation, but if other vapours are participating, one has to rely only on growth rates obtained from aerosol data.

CONCLUSIONS

The growth rate of fresh atmospheric particles can be used to get information on the condensing vapour. In addition to sulphuric acid, other vapours are needed to explain growth, at least in rural areas. Obtaining a good estimate for the growth rate is critical for the estimation of the nucleation rate. Therefore, extending the measurement range of aerosol particles to the very smallest particles is of prime importance.

Keywords: *Atmospheric Nucleation, Growth rates, Sulphuric Acid*

REFERENCES

Boy M. *et al., Atmos. Chem. Phys. 5, 863-878, (*2005*)*
Fiedler, V. *et al. Atmos. Chem. Phys. 5, 1773-1785* (2005)
Hirsikko, A., *et al. Boreal Env. Res. 10, 357-369* (2005)
Kerminen and Kulmala, *J. Aeros. Sci. 33, 609-622,* (2002)
Kulmala *et al., Tellus B53(4), 479-490* (2001)
Kulmala, M. *et al., Aerosol Science 35, 143-176.* (2004)
McMurry *et al., J. Geophys. Res., D22S02, doi: 10.1029/2005JD005901* (2005*)*
Stoltzenburg, M. R. *et al., J. Geophys. Res. 110, D22S05, doi: 10.1029/2005JD005935* (2005*)*
Weber, R. J. *et al., J. Geophys. Res.102, D4, 4375-4385* (1997)
Wehner B. *et al., Geophys. Res. Lett. 32, L17810, doi: 10.1029/2005GL023827* (2005)

The author wishes to thank the Maj and Tor Nessling foundation for financial support.

Recent Progress in Quantifying the Chemical Composition of Nanoparticles Formed by Nucleation

James N. Smith[1], **Fred L. Eisele**[1] **and Peter H. McMurry**[2]
[1]*Atmospheric Chemistry Division, National Center for Atmospheric Research, 80307, Boulder, CO, USA*
[2]*Department of Mechanical Engineering , University of Minnesota, 55455, Minneapolis, MN, USA*

INTRODUCTION

The set of chemical compounds that are expected to be in atmospheric nanoparticles are the least volatile and most difficult to measure of all atmospheric constituents. Sulphuric acid has been considered to play an important role; however, the observed linear dependence between formation rate of 3nm particles and sulphuric acid concentration calls into question whether we understand the mechanism completely and whether organic compounds may also play an important role. For almost two decades, scientists have attempted to understand the processes, and identify the species possible, for early stages of particle growth. This manuscript provides a brief history of this pursuit, focusing on measurements of sub-50 nm diameter particles. In addition, the role that the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) has played will also be discussed.

BACKGROUND

The chemical composition of newly formed particles has been studied in three ways: 1) indirectly, by measuring some other property; 2) through the use of off-line collection and analysis techniques; and 3) using real-time, online analytical techniques. Important measurements of the chemical properties of newly formed particles have been performed using tandem Nano Differential Mobility Analyzers (Nano DMAs) and condensation particle counters to investigate volatility or the uptake of water or organic compounds on size-selected aerosol. A study employing tandem Nano DMAs in urban Atlanta, GA, found that the population of 4 nm particles became less volatile and more hygroscopic following a nucleation event, which is consistent with ammonium sulfate aerosol (Sakurai et al., 2005). A similar instrument was used at Mace Head, Ireland, to study new particle formation there, where it was found that particles formed from nucleation were composed of non soluble or weakly soluble species (Vakeva et al., 2002). The growth characteristics of aerosol have been investigated using the PHA technique, which was used to infer that nanoparticles in a boreal forest region were composed primarily of organic acids (O'Dowd et al., 2002).

Offline sampling techniques involve collecting particles on a substrate, often in a size-segregated manner, for later chemical analysis. The application of offline techniques to nanoparticle composition is challenged by an inability to collect sufficient mass of these particles for analysis, often requiring longer collection times. Dimethylamine has been identified by the chemical analysis of newly formed particles collected in a low-pressure impactor in a boreal forest (Makela et al., 2001). At Mace Head, Ireland, both iodine and sulfur were found in particles with diameter below 10 nm (Makela et al., 2002), suggesting that biogenic iodine species emitted from seaweeds may be responsible for new particle formation or growth.

Online chemical analysis techniques directly analyze particles in real-time, usually by vaporizing particles by lasers or heated surfaces, ionizing the resulting gas, and injecting the ions into a mass spectrometer for analysis. These techniques are highly desirable for the study of nanoparticle composition, with both high sensitivity and short sampling times. In a study of the chemical composition of ambient ultrafine particles following nucleation events in Pittsburgh, PA, made with an Aerosol Mass Spectrometer (AMS), particles in the 18 – 33 nm diameter range were first composed of sulfate, and then after 10-40 min began to include ammonium, organics, and to a lesser degree, nitrate. In that setting, secondary organics contributed significantly to the growth of ultrafine particles in the afternoon when photochemistry was most active. In a study with an AMS made in the boreal forest at Hyytiälä, Finland, measurements of sub-100 nm particles resulting from growth over several hours following a nucleation event showed their mass to be principally, if not entirely, composed of organic species (Allan et al., 2006). The AMS was also used in chamber studies of new particle formation from the oxidation of CH_2I_2 (Jimenez et al., 2003), where they postulated that OIO is the most likely gas-phase species to produce the observed nucleation and aerosol growth. Recently a Nano-Aerosol Mass Spectrometer (NAMS) was developed to obtain the atomic composition of atmospheric nanoparticles. When employed to the study of aerosol formation from α-pinene–O_3 reactions, high C:O ratios of 1.9 and 2.5 was measured for 9 and 30 nm diameter particles, respectively (Tolocka et al., 2006).

THERMAL DESORPTION CHEMICAL IONIZATION MASS SPECTROMETER (TDCIMS)

The TDCIMS, developed specifically for characterizing the composition of freshly nucleated particles, is capable of online measurements of the molecular composition of nanoparticles as small as 5 nm in diameter with a time resolutions of ~20 minutes (Smith et al., 2004). The first field deployment of the TDCIMS was during the ANARChE field study in Atlanta, GA, during the summer of 2002. Results from that study for 6 – 15 nm diameter particles found that particles formed recently from nucleation have enhanced concentrations of ammonium and sulphate and that ammonium sulphate could account for the entire sampled nanoparticle mass. No other compounds were detected in the particles during new particle formation events (Smith et al., 2005).

Recent progress in TDCIMS development has focused primarily on organics characterization in atmospheric nanoparticles. A temperature-ramping thermal desorption scheme has been added that allows compounds to be analyzed as a function of filament temperature. This modified instrument was deployed to an urban site in Tecamac, Mexico, during the MILAGRO field study in March, 2006 and a forested site in Niwot Ridge, CO, during the CELTIC-Niwot Ridge field study in August 2006. With the improved capacity of the TDCIMS to detect organic compounds, a new picture of the composition of particles formed by nucleation is emerging. Figure 1 shows preliminary results from a "mode following experiment" in which measurements of the chemical composition of the particles in the peak of the growth mode in the size distribution were made during a new particle formation event that started at 15:00 GMT on March 16th during MILAGRO (Figure 1a). Several species were found in abundance in the particles (Figure 1b). The sulphur species (SO_2^-, SO_3^-, and SO_4^-) are surprisingly constant during the course of the event. Nitrate starts out high in the small particles and decreases in the larger particles during growth, as do peaks that we associate with organic compounds: a marker species for organics ($C_2H_2^-$), a peak associated with or organic acids ($C_2H_3O_2^-$), and a peak at 42 amu that is, as yet, unassigned. This new particle formation event on March 16 is associated with high levels of gas phase sulphur species and is believed to have been the result of a volcanic plume impact.

CONCLUSIONS

TDCIMS measurements of nanoparticle composition following new particle formation events show signals of both organics and nitrate that in some cases exceed those from sulphur species. Further analysis and measurements are forthcoming.

Keywords: *Atmospheric Nanoparticles, Nucleation, Chemical Composition*

This research was supported by the Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG-02-05ER63997 and by the NOAA Atmospheric Composition and Climate Program under grant NA05OAR4310101.

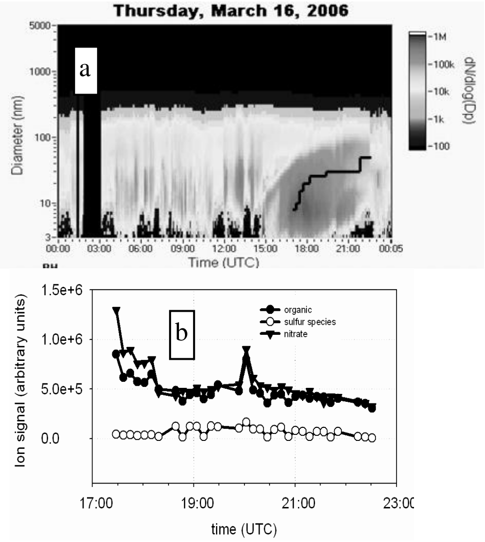

Figure 1. (a) TDCIMS "mode following experiment" (see text) during a new particle formation event observed at the T1 surface site during MILAGRO. (b) Nitrate and sulfate appeared to be the dominant species in nascent particles, while sulfate compounds remained relatively constant.

REFERENCES

Allan, J. D., Alfarra, M. R., Bower, K. N., Coe, H., Jayne, J. T., Worsnop, D. R., Aalto, P. P., Kulmala, M., Hyotylainen, T., Cavalli, F. and Laaksonen, A. (2006) *Atmos. Chem. Phys.,* **6,** 315-327.

Jimenez, J. L., Bahreini, R., Cocker, D. R., Zhuang, H., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., O'Dowd, C. D. and Hoffmann, T. (2003) *J. Geophys. Res.-Atmos.,* **108**.

Makela, J. M., Hoffmann, T., Holzke, C., Vakeva, M., Suni, T., Mattila, T., Aalto, P. P., Tapper, U., Kauppinen, E. I. and O'Dowd, C. D. (2002) *J. Geophys. Res.-Atmos.,* **107**.

Makela, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinila, K., Sillanpaa, M., Koponen, I. K., Paatero, J., Rosman, K. and Hameri, K. (2001) *Tellus Ser. B-Chem. Phys. Meteorol.,* **53,** 380-393.

O'Dowd, C. D., Aalto, P., Hameri, K., Kulmala, M. and Hoffmann, T. (2002) *Nature,* **416,** 497-498.

Sakurai, H., Fink, M. A., McMurry, P. H., Mauldin, L., Moore, K. F., Smith, J. N. and Eisele, F. L. (2005) *J. Geophys. Res.- Atmos.,* **110**.

Smith, J. N., Moore, K. F., Eisele, F. L., Voisin, D., Ghimire, A. K., Sakurai, H. and McMurry, P. H. (2005) *J. Geophys. Res.- Atmos.,* **110**.

Smith, J. N., Moore, K. F., McMurry, P. H. and Eisele, F. L. (2004) *Aerosol Sci. Technol.,* **38,** 100-110.

Tolocka, M. P., Heaton, K. J., Dreyfus, M. A., Wang, S. Y., Zordan, C. A., Saul, T. D. and Johnston, M. V. (2006) *Env. Sci. Technol.,* **40,** 1843-1848.

Vakeva, M., Hameri, K. and Aalto, P. P. (2002) *J. Geophys. Res.-Atmos.,* **107**.

The Boreal Forest Aerosol Maintained by Terpene Emissions

Peter Tunved[1], Hans-Christen Hansson[1], Veli-Matti Kerminen[2], Markku Kulmala[3], Johan Ström[1], Heikki Lihavainen[2], Yrjö Viisanen[2], Miikka Dal Maso[3], Paasi Aalto[3]
[1]*Department of Applied Environmental Science (ITM), University of Stockholm, 10691 Sweden*
[2]*Finnish Meteorological Institute (FMI), Helsinki, Finlan.*
[3]*University of Helsinki, Helsinki, Finland*

INTRODUCTION

Particle formation events are frequently being observed over boreal Scandinavia. Although the mechanisms responsible for the formation and growth of these particles are yet to parts uncertain, sulphuric acid is believed to posses a key role in the initial formation of nano-meter sized clusters. However, as the concentration of sulphuric acid rarely reaches high enough concentrations to sustain observed growth rates, other condensable compounds are a necessity to get closure between theory and observations. Organic constituents comprise a large fraction of the aerosol burden globally (Andrea and Crutzen, 1997) and there is growing evidence that naturally emitted terpenes significantly contribute to gas-to-particle formation (O'Dowd et al., 2002). The mechanism likely includes formation of condensable product from gas phase oxidation of terpenes, i.e. mono- and dicarboxylic acids. Similar compounds, or polymers thereof (Kalberer et al., 2004), could posses a low enough vapour pressure to support significant gas-to-particle formation rate in remote regions characterised by the boreal environment.

Several studies of aerosol number size distribution data from stations in Sweden and Finland have been performed (Tunved et al., 2003 and 2004a).

METHOD

Different approaches have been used to study the influence of emissions from the boreal forest. Either Lagrangian supported with detailed process models or by relating the time spent over land with typical observed features of the aerosol size distribution we are able to indirectly map the changes in size distribution properties. Based on an approach described by (European Commission, 1999) and references therein, accumulated mono-terpene emissions were estimated for each transport occasion.

RESULTS

The evolution of the size distribution as the marine to continental transition exhibit a straightforward relation to the time spent over land. The lowest average diameter is initially 20 nm. During the following 54h the mode grows up to 90nm. This corresponds to a growth rate of approximately 1.3nm/h. This pattern closely resembles the observed features of single nucleation events, indicating that nucleation event partake in the aerosol number increase during marine to continental transition of air-masses. The features are not consistent with primary emissions of small particles. The marine-to-continental transition includes a significant change in source profiles resulting in accumulating mass and number concentrations. This process is likely supported by natural emissions of terpenes. The observations are directly supported by the Lagrangian studies showing the how nucleation and subsequent growth by organics dominates the Artic air masses when transported south over the Nordic countries, while only contributing to the mass when southerly air masses are transported north over the same area (Tunved et al., 2004b and 2006a). This means that the forest at high latitudes over Scandinavia typically can support a "steady state" aerosol population representative for the typical natural source in this region (Tunved et al., 2006b).

Keywords: *Aerosol formation, Boreal forest*

REFERENCES

Andrae, M.O.and Crutzen, P.J. (1997), *Science*, 276, 1052
O'Dowd, C.D.et al, (2002), *Nature*, 416, 497-498.
Kalberer, M. et al., (2004), *Science*, 3003, 1659-1662.
Tunved, P. et al., (2003), Atm. Chem. and Phys., 3, 2183-2205
Tunved, P. et al., (2004a), Atm. Chem. and Phys., 4, 2581-2592
European Commission: Biogenic VOC emissions and photochemistry in the boreal regions of Europe – Biphorep Edited by Tuomas Laurila and Virpi Lindfors, 1999 – 158 pp., ISBN 92-828-6990-3.
Tunved, P. et al., (2004b), Atm. Chem. and Phys. Disc., 4, 7757-7794.
Tunved, P. et al., (2006a), Tellus, Vol 58, 129-140
Tunved, P. et al., (2006b), Science, April 14, 2006

This work was supported by International and national abatement strategies for transboundary air pollution (ASTA) and Nordic Center of Excellence, research unit on Biosphere - Aerosol - Cloud - Climate Interactions (BACCI).

Title: Obtaining the Diameter Growth Rate and Particle Current during Nucleation and Growth Period from Measurements of Charge Distributions and Aerosol Size Distributions

Kenjiro Iida, Mark R. Stolzenburg, and Peter H. McMurry
Department of Mechanical Engineering, University of Minnesota, 55455, Minneapolis, USA

INTRODUCTION

Measurements of + & - charged fractions (3.5-25nm), size distributions of positive and negative ions (0.4-6.3nm), and size distributions of charged and neutral particles (3 nm-5 µm) were carried out north of Mexico City in March 2006 during the MIRAGRO campaign. Fuchs surface areas and ultrafine (<10nm) particle concentrations were higher than we've observed elsewhere. Figure 1 shows a typical particle formation event observed during this study.

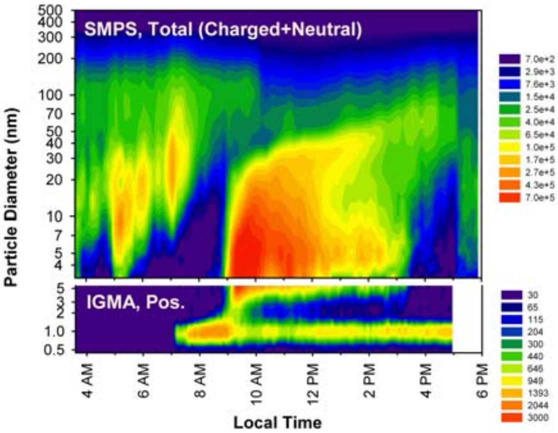

Figure 1. Contour plot of $\Delta N/\Delta \log D_P$ of total (charged and neutral particles (above) and small and intermediate ions (below) measured on March 21st, 2006 north of Mexico City.

It was generally difficult to obtain the diameter growth rate, dD_P/dt, from the measured particle size distribution during nucleation events in Mexico City since the growth of modal sizes was not clearly visible. In order to overcome this problem, we developed a method to estimate dD_P/dt from the measured charged fraction, f, in the 3.5-15.5nm range assuming that the measured profile of f vs size, D_P, can be characterized by the steady state charge distribution undergoing condensational growth and collisions with ions.

THEORY

In order to make the method simple and transparent, the concentration and mobility of positive and negative ions are assumed to be equal: $c_{ion}^{+} \approx c_{ion}^{-} \equiv c_{ion}$ and $Z_{ion}^{+} \approx Z_{ion}^{-} \equiv Z_{ion}$. The initial charged fraction of positively and negatively charged nucleated particles, which are assumed to be ~1nm, are equal, $f_{1nm}^{+} \approx f_{1nm}^{-} \equiv f_{1nm}$. The under these assumptions, the governing equation of the steady state charge fraction, f, is given by

$$\frac{d\left(f\tilde{\Omega}\right)}{d\tilde{D}_P} = \frac{1}{\tilde{G}}\left(\tilde{\beta}_0(1-2f)-\tilde{\beta}_1 f\right). \tag{1}$$

where $\tilde{\beta}$ is the dimensionless ion-aerosol attachment coefficient defined by $\tilde{\beta} = \beta/\beta^{*}$, where β^{*} is chosen to be 2-3×10^{-8} cm^3/s. $\tilde{D}_P$ is the dimensionless size defined as $\tilde{D}_P = (D_P - D_{P0})/\Delta D_P$, where D_{P0} is initial size (assumed to be 1nm), and ΔD_P is the size range that particles grow through (15.5-1.0=14.5nm, where 15.5 nm is the upper size at which charged fractions were measured). $\tilde{G}$ is the dimensionless growth rate defined as

$$\tilde{G} = \frac{(dD_P/dt)}{\Delta D_P \beta_0^{*} c_{ion}}. \tag{2}$$

The value of $\tilde{G}$ ranges from 0.25-250 over conditions in the atmospheric boundary layer. $\tilde{\Omega}$ is the dimensionless enhancement factor in condensation due to charge-dipole interaction (*Tammet and Kulmala* 2005). According to Eqn 1, the profile of f vs. D_P is determined by a unique set of $\tilde{G}$ and f_{1nm}. Further theoretical analysis showed that $\tilde{G}$ essentially determines the f vs. D_P in 3.5-15.5nm as f_{1nm} approaches zero.

VALIDATION OF THE THEORY

First, the theory based on the steady state assumption is qualitatively verified by our measurements. In our previous study, we showed that nucleated particles "remember" their initial charge state during their growth up to ~15 nm (*Iida et al.,* 2006). Figure 2 shows the measured charged fraction normalized by the stationary state value of Fuchs (1963) within the 3.5-15.5nm range measured during three nucleation events observed in either

Boulder CO or Mexico City. The modal growth rate could be accurately obtained from the measured particle size distribution during those nucleation events; therefore, the values of $\widetilde{G}$ can be calculated independently from the charged fraction measurements. As shown in the figure, the profile of f vs. D_P becomes more undercharged as the value of $\widetilde{G}$ increases. In all cases, the initial charge states of nucleated particles are expected to be almost all neutral and more clearly remembered as $\widetilde{G}$ increases.

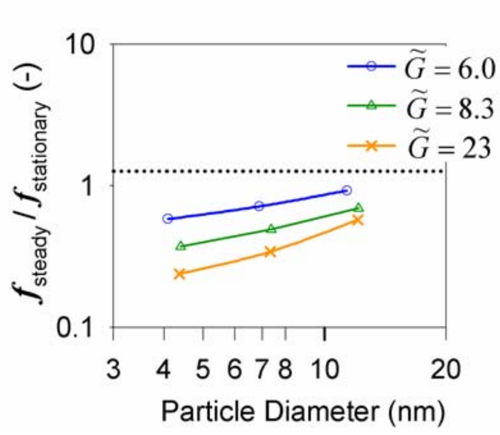

Figure 2. Measured charged fractions in the 3.5-15.5nm range during three nucleation events in either Boulder CO or Mexico City from which the modal growth rates are obtained. The value of $\widetilde{G}$ was calculated using observed modal growth rate and ion concentration and mobility.

Second, the theory is quantitatively verified by our measurements. The calculated f vs D_p were fitted to the measured values during nucleation and growth period by changing the input $\widetilde{G}$ and f_{1nm}. Then, estimated dD_p / dt from the $\widetilde{G}$ are compared to the observed modal growth rate during nucleation events (Figure 3). The six nucleation events observed in either Boulder CO or Mexico City were analyzed. As shown in the figure, the value of dD_p / dt inferred from the steady-state assumption agrees reasonably well with the observed modal growth rates over the 3.5 to 23 nm/hr range.

APPLICATION OF THE THEORY

Using the steady-state approach introduced above, the growth rate during particle formation event on March 21st 2006 was estimated. Table 1 summarizes the results. The nucleated particles are essentially all neutral, and the estimated particle current at 4.3nm and 1nm for a typically observed nucleation event are ~300 and ~1800 $cm^{-3}s^{-1}$, respectively, indicating that particle formation rate in the atmospheric boundary layer of Mexico City is unusually high.

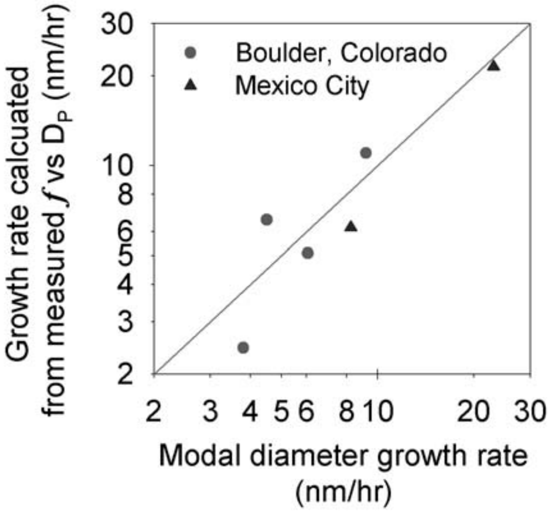

Figure 3: Comparison of diameter growth rates calculated from measured charge fractions with observed growth rates of modal diameters in 3.5-15.5nm range.

Table 1. Summary of analysis of the nucleation event observed on March 21st, 2006 at Mexico City

Parameter	Values
f_{1nm}	Essentially zero
dD_p / dt	~ 22 nm/hr
Particle Current, J, 3.5-5.7nm range	~300 cm^{-3} s^{-1}
Particle Current, J, at 1nm	~1800 cm^{-3} s^{-1}
SO_2 concentration during nucleation period	40-50 ppb

REFERENCES

Fuchs, N. A. (1963), On the stationary charge distribution on aerosol particles in a bipolar ionic atmosphere, *Geofisica Pure e applicata, 56*, 185-193.

Iida, K., R. M. Stolzenburg, P. H. McMurry, M. Dunn, J. N. Smith, F. Eisele and P. Keady (2006), Contribution of ion-induced nucleation to new particle formation: methodology and its application to atmospheric observations in boulder, CO, *J. Geophys. Res., (Accepted)*,

Tammet, H. and M. Kulmala (2005), Simulation tool for atmospheric aerosol nucleation bursts, *J. Aerosol Sci., 36*, 2, 173-196.

Observations of ultrafine particles in combination with different boundary layer processes

Birgit Wehner[1], **Holger Siebert**[1], **Alfred Wiedensohler**[1], **and Frank Stratmann**[1]
[1]*Leibniz-Institute for Tropospheric Research, 04318 Leipzig, Germany*

INTRODUCTION

New particle formation events have been observed at various locations all over the world. Although these ultrafine particles appear to be caused by nucleation, the detailed process and related precursor gases are still unclear. Few field studies indicate that the occurrence of new particles is related to the boundary layer development, probably due to turbulent mixing processes. However, most of these studies were either restricted to ground-based particle measurements or based on aircraft measurements with poor spatial resolution. But detailed information about the vertical profiles of ultrafine particle are still rare.

Here, high resolution measurements made with a tethered balloon-borne payload during the SATURN campaign (Stratmann et al., 2003) are presented. Vertical profiles with enhanced ultrafine particle concentration in different heights indicate nucleation events. The influence of the planetary boundary layer development and related phenomena on new particle formation is discussed.

EXPERIMENTAL

Measurements have been performed using a tethered balloon which lifted the instrumental payload ACTOS (Airborne Cloud Turbulence Observation System) up to a height of 1300 above ground level (agl). ACTOS is an autonomous system, which is equipped with sensors to measure the meteorological standard parameters (three-dimensional wind vector, static air temperature, and humidity) with high temporal (100 Hz sampling frequency) and spatial resolution. Furthermore, two Condensation Particle Counters (CPCs, TSI-model 3762) with different lower detection limits provided particle number concentration in two size ranges. From the difference, the concentration of the ultrafine particles $N_{5\text{-}10}$ in the size range between 5 and 10 nm was derived. In addition, SO_2 gas concentrations have been measured (THERMO ENVIRONMENTAL, Model 43C) with a time resolution of 10 s.

A more detailed description of ACTOS and the tethered balloon system can be found in Siebert et al. (2003), details of the aerosol measurements on ACTOS are described in Stratmann et al. (2003) and Siebert et al. (2004).

Measurements during SATURN 2002 have been performed in Melpitz (42 km north-east of Leipzig, Germany). The site is located on a flat meadow, surrounded by agricultural land and forests.

RESULTS

Vertical profiles of particle number concentrations and meteorological parameters have been measured on several days in June 2002. Here, two case studies will be presented illustrating the vertical variability of ultrafine particle concentration.

i) Nucleation in the residual layer

Figure 1 shows three selected vertical profiles of $N_{5\text{-}10}$ (left panel) and of potential temperature T_{pot} (right panel) measured on June 3 between 5:35 and 11:30 CEST over Melpitz. The times represent a mean time for the respective ascent or descent, which took 10 – 20 min with a typical climb rate of the balloon of 1 to 2 m s^{-1}.

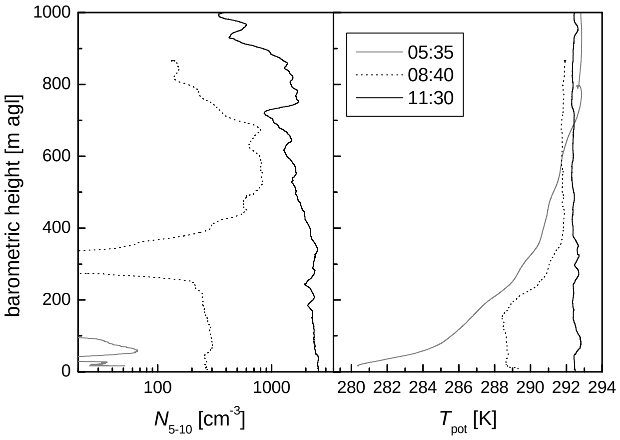

Figure 1. Selected vertical profiles of $N_{5\text{-}10}$ in the size range of 5 - 10 nm (left side) and potential Temperature T_{pot} (right side) measured on June 3 in Melpitz. Times are in CEST and valid for the mean of profile.

During the first ascent around 5:35 CEST $N_{5\text{-}10}$ no significant concentrations of ultrafine particles were observed within the lowest 1000 m. Only in the lowest 100 m values up to 50 cm^{-3} were measured. T_{pot} increased continuously up to a height of 700 m indicating a strong temperature inversion near ground level. The measurement at 8:40 CEST shows a temperature inversion between 200 and 350 m and $N_{5\text{-}10}$ of less than 300 cm^{-3} below the inversion but up to 800 cm^{-3} above. Thus, formation of ultrafine particles started independently at different heights because the strong inversion layer prevents mixing between ground based and overlaying air masses. $N_{5\text{-}10}$ was significantly higher above the inversion indicating new particle formation within this layer. At 11:30 the temperature inversion had disappeared and a well mixed boundary layer has been developed.

Then, $N_{5\text{-}10}$ was nearly constant over the entire PBL, thus the newly formed particles from above were mixed downwards.

ii) Nucleation below a low-level-jet

Figure 2 shows vertical profiles of $N_{5\text{-}10}$ (left panel), horizontal wind speed u (middle), and SO_2 concentration (right panel) up to a height of 700 m measured on June 4 between 8:00 and 10:00 CEST.

During the first measurement at 8:15 CEST u shows a clear local maximum of 8 m s^{-1} in a height of 280 m indicating a low level jet (LLJ). At the same time SO_2 shows a maximum slightly below the wind maximum indicating advection of SO_2 in connection with the LLJ.

$N_{5\text{-}10}$ shows no significant concentrations above the LLJ, but reaches nearly 100 cm^{-3} at the lower edge of the LLJ. The following sounding at 9:00 shows the LLJ nearly at the same height, $N_{5\text{-}10}$ is increased compared to the last profile.

At 9:45 the LLJ was nearly disappeared and the maximum in $N_{5\text{-}10}$ covered a broader layer between 100 and 300 m.

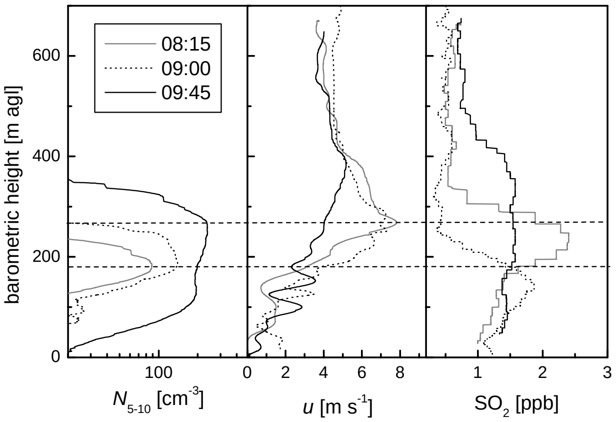

Figure 2. Vertical profiles of $N_{5\text{-}10}$ in the size range of 5 - 10 nm (left side), horizontal wind speed u (middle), and SO_2 concentration (right side) measured on June 4 in Melpitz. Times are in CEST and valid for the mean of profile.

CONCLUSIONS

Several examples of significantly increased concentrations of ultrafine particles in different heights of the PBL have been found during the SATURN campaign. Two examples have been shown here: new particle formation above an inversion layer followed by the observation of ultrafine particles all over the mixing layer after breaking up of the inversion.

In the second case significantly enhanced concentrations of SO_2, which was advected by a low level jet, correlates with the increased concentrations of ultrafine particles. Furthermore, turbulent mixing at the lower boundary of the LLJ leads to turbulent mixing with lower air masses which might enhance the nucleation process. At this time no ultrafine particles were found at ground level.

In addition to these two presented cases Siebert et al. (2004) detected ultrafine particles near the inversion layer. Turbulent downward transport has been suggested to explain the following occurrence of ultrafine particles near the ground.

All these observations corroborate the hypothesis that new particle formation events often depend on different mixing and other processes which are typical for the PBL development (Bigg, 1997, Nilsson et al., 2001). Due to mixing of different air masses conditions can be created which are favourable for nucleation. Furthermore, under certain circumstance ground-based observations alone are not able to shed light on the question which processes led to nucleation.

Thus, airborne measurements of ultrafine particles, meteorology, and other related parameters as trace gases with high time resolution are necessary and planned. New instrumentation for high resolution measurements with a helicopter-borne version of ACTOS are under development.

Keywords: *planetary boundary layer, nucleation, new particle formation*

REFERENCES

Bigg, E.K. (1997) A mechanism for the formation of new particles in the atmosphere, *Atmospheric Research*, 43: 129-137.

Nilsson, E.D., Ü. Rannik, M. Kulmala, G. Buzorius, and C.D. O'Dowd (2001) Effects of continental boundary layer evolution, convection, turbulence and entrainment, on aerosol formation, *tellus*, 53B: 441-461.

Siebert, H., M. Wendisch, T. Conrath, U. Teichmann and J. Heintzenberg (2003) A new tethered balloon-borne payload for fine-scale observations in the cloudy boundary layer. *Boundary-Layer Meteorol.*, 106, 461 - 482.

Siebert, H., F. Stratmann and B. Wehner (2004) First observations of increased ultrafine particle number concentrations near the inversion of a continental planetary boundary layer and its relation to ground-based measurements. *Geophys. Res. Lett.*, 31(L09102), doi: 10.1029/2003GL019086.

Stratmann, F., H. Siebert, G. Spindler, B. Wehner, D. Althausen, J. Heintzenberg, O. Hellmuth, R. Rinke, U. Schmieder, C. Seidel, T. Tuch, U. Uhrner, A. Wiedensohler, U. Wandinger, M. Wendisch, D. Schell, A. Stohl (2003) New-particle formation events in a continental boundary layer: First results from the SATURN experiment, *Atmos. Chem. Phys.*, 3, 1445 - 1459.

Nucleation Events at a high Alpine Site: Particle Growth and Nucleation Rates

Bart Verheggen [1*], Ernest Weingartner [1], Julie Cozic [1], Marko Vana [2], Pasi Aalto [2], Anne Hirsikko [2], Markku Kulmala [2] and Urs Baltensperger [1]

[1]*Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
[2]*Department of Physical Sciences, University of Helsinki, 00014 Helsinki, Finland*
[*]*Currently at Institute for Atmospheric and Climate Sciences, ETH, 8092 Zurich, Switzerland*

INTRODUCTION

Atmospheric nucleation events were regularly observed during the fourth Cloud and Aerosol Characterization Experiment (CLACE 4), conducted at the Swiss high alpine research station Jungfraujoch in winter 2005. The measurement site (3580 metres altitude) is far removed from strong pollution sources and is deemed representative of the continental lower free troposphere. The station is regularly engulfed in clouds (37% of the time based on a year long survey reported by Baltensperger et al. (1998). These characteristics make the Jungfraujoch well suited to investigate atmospheric aerosols (e.g. Weingartner et al., 1999) and mixed phase clouds from a ground based platform (e.g. Henning et al., 2004). The measured aerosol size distributions were analyzed to determine empirical nucleation and growth rates using the method of Verheggen and Mozurkewich (2006).

MEASUREMENTS

The aerosol size distribution was measured both indoors under dry conditions (due to heating to room temperature) and outdoors under ambient conditions (temperatures between -28 and -12 °C). The outdoor Scanning Mobility Particle Sizer (SMPS) measured the size range from 4 to 100 nm (ambient) diameter, while the indoor spectrum covered the range from 18 to 800 nm (dry) diameter. The indoor measurements were complemented by a nano-SMPS (size range from 4 to 100 nm diameter) on loan from TSI Inc. for a duration of 10 days. The total particle number concentration (D_p > 10 nm) was measured both in- and outdoors by TSI 3010 condensation particle counters. The measured size distributions were combined prior to data analysis, taking into account the hygroscopic size shift and particle losses. An Air Ion Spectrometer (AIS) was operated indoors to measure charged clusters and particles from 0.5 to 40 nm diameter.

RESULTS

Several nucleation events were observed to occur during the 5-week intensive measurement period. These were analyzed to derive empirical particle nucleation and growth rates using a recently developed inverse modeling procedure called PARGAN (Verheggen and Mozurkewich, 2006). The growth rate is determined by non-linear regression analysis of the General Dynamic Equation using only the measured aerosol size distributions as input. This allows the growth rate to be determined with a higher time-resolution than can be deduced from inspecting contour plots ("banana-plots"). These growth rates are used to estimate the time of formation of recently nucleated particles (where the critical cluster is assumed to be 1 nm diameter). The nucleation rate is determined by correcting for the particle losses that have occurred between time of nucleation and time of measurement due to coagulation.

Figure 1 shows a contourplot of size distributions during such an event; resulting growth and nucleation rates are shown in Figure 2.

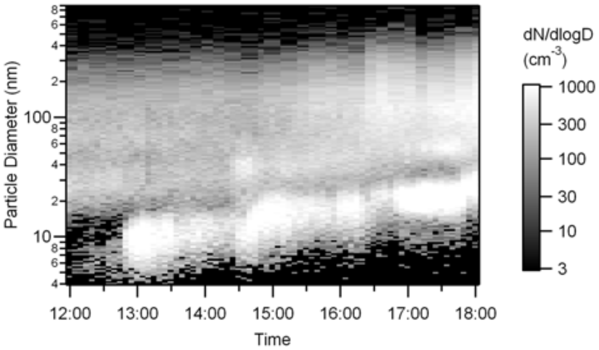

Figure 1. Measured aerosol size distributions during a nucleation event on March 6, 2005.

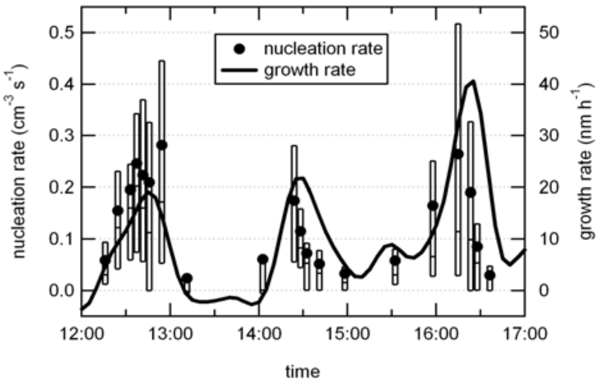

Figure 2. Empirically determined diameter growth rates (solid line) and 1-nm nucleation rates (symbols) for the event depicted in Figure 1. Solid circles denote the average while boxes denote the 25, 50 and 75 percentile values of the nucleation rate.

The kinetically limited particle growth rate is proportional to the concentration of the condensing species. It is therefore to be expected that the nucleation and growth rate reach their maximum at approximately the same time, if the same species contributes to both processes. The nucleation rate is relatively low (< 1 cm^{-3} s^{-1}), while the growth rate reaches relatively high values of up to 20-40 nm h^{-1}. This suggests that H_2SO_4 can not be the main contributor to condensation, since it has a very high nucleation potential.

Nucleation events usually occurred during relatively clean and clear sky conditions, often soon after cloud evaporation. However, the event depicted in Figures 1 and 2 occurred during the presence of a mixed-phase cloud. The combination of a high actinic flux, a high relative humidity and evaporating droplets may have created a favorable environment for nucleation. The presence of ice probably contributed to the evaporation of liquid droplets via the Wegener-Bergeron-Findeisen mechanism. This led to the release of semi-volatile material into the gas phase, where it could contribute to particle nucleation and growth. During this event the aerosol was found to be overcharged (compared to equilibrium), suggesting that ions may have played a role in the nucleation process.

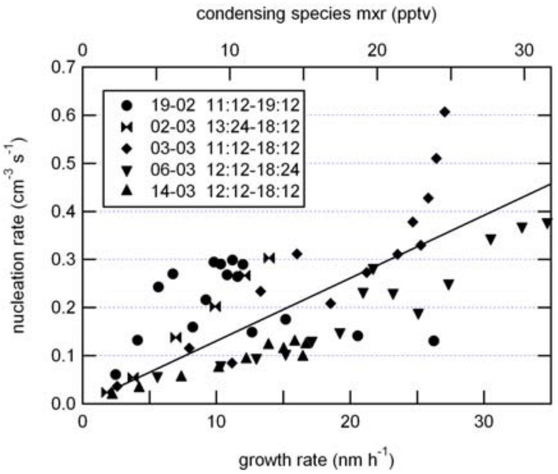

Figure 3. Empirical nucleation and growth rates (and equivalent condensing vapor concentration) determined for 5 different events. Both are determined from the measured size distributions using the inverse modeling procedure PARGAN. Each symbol is based on approximately the same amount of data (between 82 and 102 size bins, each of which is tracked backwards to its time of formation).

The same analysis was performed for five nucleation events. The resulting nucleation rates are shown in Figure 3 as a function of the particle growth rate and the equivalent mixing ratio of condensing vapor.

A similar relation between the nucleation rate and the growth rate (and thus vapor concentration) was found for all these events. This relation appears to be close to linear, as seen from the linear fit through the average values (black line). If the same (group of) species was responsible for nucleation and growth, this is more consistent with an activation mechanism or kinetic (barrierless) nucleation than with themodynamically limited nucleation.

CONCLUSIONS

Nucleation events as observed from a high mountain platform were analyzed to determine empirical particle nucleation and growth rates. The relation between the nucleation and growth rate is nearly linear. Nucleation was observed to occur both during the absence and the presence of clouds. Though nucleation rates were found to be small, their regular occurrence suggest that nucleation in the lower free troposphere could contribute significantly to the aerosol number concentration budget.

Keywords: *Atmospheric Nucleation, Free Tropospheric Aerosols, Cloud/Fog Aerosol Interactions*

REFERENCES

Baltensperger, U., M. Schwikowski, D.T. Jost, S. Nyeki, H.W. Gäggeler, and O. Poulida, Scavenging of atmospheric constituents in mixed phase clouds at the high-alpine site Jungfraujoch part I: Basic concept and aerosol scavenging by clouds, *Atmos. Env.*, 32 (23), 3975-3983, 1998.

Verheggen, B., and Mozurkewich M. An inverse modeling procedure to determine particle growth and nucleation rates from measured aerosol size distributions, *Atmos. Chem. Phys.*, *6*, 2927-2942, 2006.

Henning, S., S. Bojinski, K. Diehl, S. Ghan, S. Nyeki, E. Weingartner, S. Wurzler, and U. Baltensperger, Aerosol partitioning in natural mixed-phase clouds, *Geophys. Res. Lett.*, 31 (6), 2004.

Weingartner, E., S. Nyeki, and U. Baltensperger, Seasonal and diurnal variation of aerosol size distributions (10 < D < 750 nm) at a high-alpine site (Jungfraujoch 3580 m asl), *J. Geophys. Res.*, 104 (D21), 26809-26820, 1999.

Acknowledgements: This work was supported by the Swiss Meteorological Institute (Global Atmosphere Watch program). We thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG) for the opportunity to perform experiments at the Jungfraujoch.

Measurements and Modeling of Atmospheric Homogeneous Nucleation

Alicia K. Pettibone[1], William Eichinger[2], Spyros N. Pandis[3], Charles O. Stanier[1]
[1]Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City IA, 52242 USA
[2]Department of Civil and Environmental Engineering, University of Iowa, Iowa City IA, 52242 USA
[2]Department of Chemical Engineering, University of Patras, Patras, Greece

INTRODUCTION

The creation of new atmospheric particles via nucleation is an important source of atmospheric particles and may influence climate by altering the aerosol size distribution and the related direct and indirect aerosol effects. While there are many possible mechanisms to describe the process of nucleation and subsequent particle growth, there are still significant gaps in the knowledge of new particle formation. In particular, we are interested in determining the strength (in terms of particle formation rate and growth rate), spatial coverage, and frequency of events.

DATA SETS TO BE DISCUSSED

We will integrate our recent field studies during summer 2005 in Bondville Illinois (midwestern U.S.) and spring 2006 in Mexico City with previous measurements from Pittsburgh PA to investigate the intensity, frequency, and temporal patterns of new particle formation in these different locations. In each case, particle size distributions measured by SMPS are supplemented by additional meteorological, aerosol-phase, and gas-phase data. In Pittsburgh, a wide variety of aerosol parameters and gas measurements were available due to the Pittsburgh Supersite Program. In Bondville, collocated SO_2 and meteorology were measured, and in Mexico collocated elastic LIDAR is used to look at the relationship between new particle formation and vertical transport.

RESULTS AND DISCUSSION

Regional new particle formation events are most common in Pittsburgh (~3 of 10 days averaged over 1 year). Sampling duration was not long enough in Bondville (2 months) or Mexico City (1 month) to establish an overall frequency, but particle formation events appear to be somewhat less frequent (than Pittsburgh) in both locations. Mexico City new particle formation has been investigated previously by Dunn et al. (2004). In Bondville IL, which has lower SO_2 concentrations than Pittsburgh or Mexico City, growth rates are lower. In all three locations, particle formation events often occur simultaneously with rapid increase in boundary layer height. However, this is not always the case. In all locations, events also occur before rapid increase in the boundary layer height.

In Mexico City, the role of the boundary layer and residual layer in new particle formation appears to be very important. The Mexico City basin has been shown to have strong thermally and topographically driven circulations (Doran et al., 1998). The connection of this unique meteorology to new particle formation is potentially mportant because it may give clues as to the mechanism(s) at work for formation and growth, determine the spatial coverage, and explain the observance of formation events from ground-based samplers.

On several of the study days in Mexico City, rapid decreases in PM concentrations in the early afternoon are simultaneous with rapid increase in boundary layer height, high friction velocities, and the appearance of a newly formed and growing sub-50 nm mode in the number size distribution. We analyze these days by looking at ground based size distributions, collocated elastic LIDAR measurements, and collocated wind profiler readings.

We also conduct box modeling of particle formation events at several of the locations, using a ternary ammonia-sulfuric acid-water parameterization. This shows that ammonia is likely the limiting reagent in the particle formation process in Pittsburgh in summer. Changes in NH_3 and SO_2 concentrations due to the Clean Air Act and Clear Skies Initiative are likely to influence particle formation activity in the Eastern U.S. by changing the balance between basic and acidic species.

Keywords: *Nucleation Measurements, New Particle Formation and Growth*

REFERENCES

Doran, J. C., S. Abbott, et al. (1998), The IMADA-AVER boundary layer experiment in the Mexico City area, *Bulletin Of The American Meteorological Society* **79**(11), 2497-2508.

Dunn, M. J., J. L. Jimenez, et al. (2004), Measurements of Mexico City nanoparticle size distributions: Observations of new particle formation and growth, *Geophysical Research Letters* **31**(10).

This work was supported by the University of Iowa, Vice President for Research.

New Particle Formation in the Upper Troposphere and Lower Stratosphere: Air Mixing, Vertical Convection, and Photochemistry

Shan-Hu Lee[1], David R. Benson[1], Li-Hao Young[1], James C. Wilson[2], William Montanaro[1], Jorgen Jensen[3], Jeff Stith[3], Christopher A. Davis[4], Teresa L. Campos[3], David Rogers[3], and William A. Cooper[3]

[1] *Kent State University, Department of Chemistry, Kent, Ohio, USA*
[2] *University of Denver, Department of Engineering, Denver, Colorado, USA*
[3] *National Center for Atmospheric Research, Research Aviation Facility, Broomfield, Colorado, USA*
[4] *National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, Colorado, USA*

The upper troposphere and lower stratosphere (UT/LS) is a source of new particle formation. In particular, particle nucleation can be stronger in the tropopause region because of low temperatures and air mixing actively occurring in this region. There has been also controversy on the effects of surface area on new particle formation in the UT/LS.

Here we report our recent results of new particle formation observed at the latitudes from 18 °N – 62 ºN and altitudes up to 16 km in December 2005 during the High-performance Instrumented Airborne Platform for Environmental Research (HIAPER) Progressive Science Missions (ten research flights, in total). Aerosol sizes and concentrations in the diameter range from 4 to 1000 nm were measured with the University of Denver nuclei mode aerosol sizing spectrometer (NMASS) and forward cavity aerosol spectrometer (FCAS).

Our observations show that frequent new particle formation takes place at a large spatial and temporal scale in the low- and mid-laltitude UT/LS, consistent with other observations [e.g., Minikin et al., Twohy et al., 2002; Hermann et al., 2003; Lee et al., 2003]. Strong new particle formation events are also often accompanied with vertical convection that brings aerosol precursors (originating from the ground level) up to higher altitudes. Strong new particle formation was also observed during the midlatiutude tropopause folding because of the stratosphere and troposphere air exchange, consistent with the modeling predictions of sulfuric acid and water binary homogeneous nucleation showing that air mixing can enhance nucleation rates significantly [Nilsson et al., 2000]. Relatively high number concentrations of ultrafine particles were measured during nighttime (sometimes even higher than during daytime), suggesting night time sulfuric acid formation as shown by other field studies [Mauldin et al., 2003]. Also, the measured ultrafine particle concentrations are a function of the ratio of average sunlight hour over surface area of the air mass, rather than of surface area only, consistent with Lee et al. (2003).

These results are also described in detail in elsewhere [D. R. Benson et al., Aerosol size distributions measured in the UT/LS during the HIAPER Progressive Science Missions, manuscript in preparation; L.-H. Young et al., Enhanced new particle formation observed during the midlatitude tropopause folding, manuscript in preparation]. A poster by D. R. Benson et al. in the IAC 2006 (*p. 1397*) also describes these results.

Keywords: *New particle formation, Nucleation, Upper troposphere and lower stratosphere, air mixing*

REFERENCES

Hermann, M. et al. (2003), Meridional distributions of aerosol particle number concentrations in the upper troposphere and lower stratosphere obtained by Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) flights, *J. Geophys. Res.*, **108**, doi:10.1029/2001JD001077.

Lee, S. H. et al. (2003), Particle formation by ion nucleation in the upper troposphere and lower stratosphere, *Science*, 301, 1886–1889.

Mauldin R. L. III et al. (2003), Measurements of OH, H_2SO4, and MSA during Tropospheric Ozone Production about the Spring Equinox (TOPSE), *J. Geophys. Res.,* 108 doi:10.1029/2002JD002295.

Minikin, A., et al. (2003), Aircraft observations of the upper tropospheric fine particle aerosol in the northern and southern hemispheres at midlatitudes, *Geophys. Res. Lett.*, **30**, Doi:10.1029/2002GL016458.

Nilsson, E. D., L. Pirjora, and M. Kulmala (2000), The effect of atmospheric waves on aerosol nucleation and size distribution, *J. Geophys. Res.*, **105**, 19917-19926.

Twohy, C. H. et al. (2002), Deep convection as a source of new particles in the midlatitude upper troposphere, *J. Geophys. Res.*, **107**, Doi:10.1029/2001JD000323, 2002.

This study is supported by the National Science Foundation fund awarded to Kent State University (ATM-0507709) and Kent State startup fund to SHL. We also thank the pilots, scientists and engineers involved in the HIAPER Progressive Science Missions.

Growth Rates of Freshly Nucleated Atmospheric Particles in Atlanta

Mark R. Stolzenburg[1], Peter H. McMurry[1], Hiromu Sakurai[1], James N. Smith[2], R. Lee Mauldin III[2], Fred L.Eisele[2] and Charles F. Clement[3]
[1] Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455 USA
[2] Atmospheric Chemistry Division., National Center for Atmospheric Research, Boulder, CO 80307 USA
[3] Enviros-Quantisci, Wantage, Oxon OX12 9EU, UK

During the Atlanta ANARChE Study of July-August, 2002, atmospheric aerosol size distributions from 3 to 2000 nm were measured continuously with 5-minute resolution. Sulfuric acid vapor concentrations were also measured. During regional nucleation events these data showed the presence of a nucleation mode that grew at rates ranging from 3 to 20 nm h^{-1}.

Figure 1 shows measured modal growth rates of nucleation mode particles during regional nucleation events versus measured sulfuric acid vapor concentrations from this and previous studies. Calculated contributions of sulfuric acid condensation to growth are also shown. Note that measured growth rates are almost always greater than can be explained by sulfuric acid condensation.

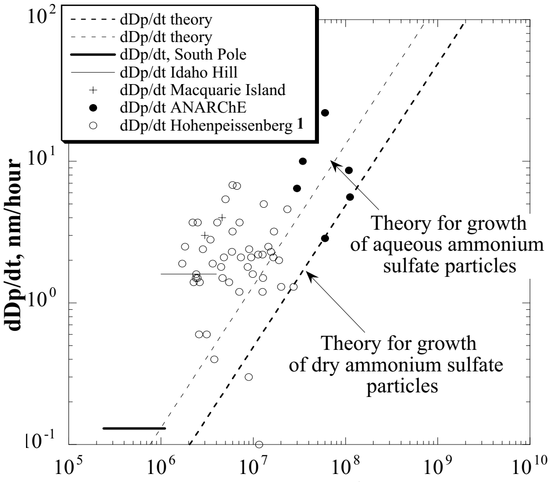

Figure 1[2]: Measured nucleation mode growth rates and calculated H_2SO_4 condensation growth rates versus H_2SO_4 vapor concentration.

In this paper we compare these measured modal growth rates with calculated rates that account for sulfuric acid condensation as well as intramodal coagulation of nucleation mode particles, and extramodal coagulation of nucleation mode particles with preexisting particles. Data collected during six time intervals were amenable to analysis.

Calculated and measured growth rates (Figure 2) were in reasonable agreement for the four events (7/31, 8/01, 8/05 a.m., 8/10) that involved growth below 40 nm (ratios of measured to calculated growth rates = 1.0, 2.1, 0.68, 0.60). Two of the three afternoon events (8/05 p.m., 8/19) involved growth above 40 nm, and in these cases measured rates substantially exceeded calculated rates by factors of four to five, suggesting that our model did not account for all growth processes.

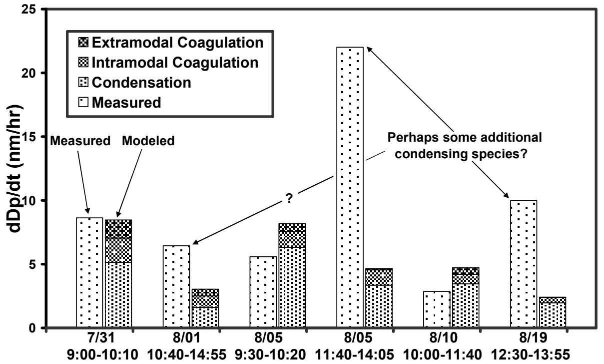

Figure 2[2]: Measured and modeled nucleation mode growth rates for ANARChE data.

We also compared observed rates of change in nucleation mode number concentration with calculated coagulation rates. During the sub-40 nm growth events particle concentrations decreased at rates that were significantly below calculated coagulation rates or even increased, suggesting that a source of particles was present. Measured size distributions suggest that particle production by nucleation continued during these events and contributed to this discrepancy. Concentrations during the super-40 nm events decreased at rates that exceeded calculated coagulation rates.

In conclusion, coagulation can account for some of the discrepancies between measured and calculated H_2SO_4 condensation modal growth rates that have been reported previously. Nucleation may continue during growth up to 40 nm. Other species may contribute to growth above 40 nm.

[1] Birmili, W., H. Berresheim, C. Plass-Dulmer, T. Elste, S. Gilge, A. Wiedensohler and U. Uhrner (2003), *Atmospheric Chemistry And Physics*, *3*: 361-376.

[2] Stolzenburg, M., P. McMurry, H. Sakurai, J. Smith, R.L. Mauldin, F. Eisele, C. Clement (2005), *J. Geophys. Res.*, *110*, D22S05.

Aerosol Formation from Isoprene: Determination of Particle Nucleation and Growth Rates from measured Size Distributions.

Bart Verheggen[*], **Jonathan Duplissy**, **Axel Metzger**, **Joseph Dommen**, **Ernest Weingartner**, **Andre Prevot**, **Urs Baltensperger**
Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[*]*Currently at Institute for Atmospheric and Climate Sciences, ETH, 8092 Zurich, Switzerland*

INTRODUCTION

Isoprene is one of the most abundant non-methane hydrocarbons emitted into the troposphere. It is therefore of great interest to investigate the degree to which isoprene may contribute to the formation of Secondary Organic Aerosol (SOA). Measurements of aerosol formation and growth following isoprene oxidation have been performed in the PSI smog chamber to address this issue. Using only the measured aerosol size distributions as input, we determined empirical particle nucleation and growth rates. We briefly review this method and present major results pertaining to the isoprene SOA formation.

MEASUREMENTS

Photooxidation experiments were carried out in a 27 m^3 Teflon chamber at 20°C (Paulsen et al., 2005). A known amount of isoprene (Fluka, 99.5%) was evaporated in a heated glass sampling bulb and continuously flushed with pure air into the chamber and allowed to equilibrate for 30 min. Four xenon arc lamps were used to simulate the solar light spectrum and start the photochemistry.

Aerosol size distributions were measured using a twin-SMPS system, one with a short classifier and a TSI 3786 UWCPC (4-150 nm) and one with a long classifier and a TSI 3022 CPC (16-700 nm). From these we made composite size distributions covering the whole size range from 4 to 700 nm diameter which we used for further analysis.

The experiment was started by producing particles through ozonolysis of isoprene. This aerosol was diluted to reduce the particle concentration to around 500 cm^{-3}. We then injected 350 ppbv of isoprene in the presence of NO and turned on all chamber lights. An hour later, the pre-existing particle mode started to significantly grow in size, indicative of condensation. Another two hours later a modest nucleation event occurred, producing approximately 4000 new particles cm^{-3}. A contourplot of the measured size distributions is shown in Figure 1.

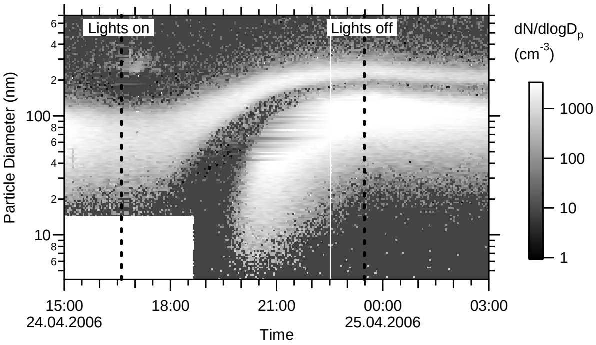

Figure 1. Measured size distributions following isoprene ozonolysis in the morning (pre-existing mode) and isoprene photo-oxidation in the evening (nucleation mode).

ANALYSIS PROCEDURE

Nucleation and growth rates were determined from the measured size distributions using a recently developed inverse modeling procedure called PARGAN (Particle Growth and Nucleation) (Verheggen and Mozurkewich, 2006). A highly time-resolved (size dependent) particle growth rate is found by regression analysis of the General Dynamic Equation (GDE). These empirical growth rates are then used to estimate the time of nucleation for particles in each measured size bin, defined as the time when their calculated diameter surpassed 1 nm. Their number density at the time and size of nucleation is determined by integrating the particle losses that occurred in the time interval between nucleation and measurement. The nucleation rate is then given by the rate at which particles grow past the critical cluster size, assumed to be 1 nm diameter.

RESULTS

There are some advantages to having pre-existing aerosol present during nucleation: It allows the particle growth rate –and thus the time of nucleation– to be determined before the nucleated particles grew to a detectable size. It is also more representative of the atmosphere, where aerosol is always present when nucleation occurs. The diameter growth rate determined using PARGAN is shown in Figure 2. The growth rate is proportional to the concentration of the condensing species above saturation; its equivalent value is given on the right axis.

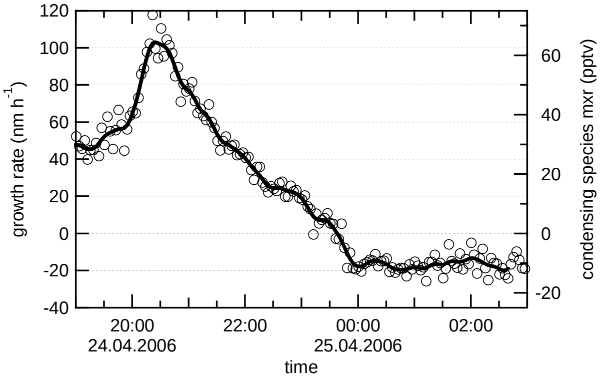

Figure 2. Particle growth rate during photo-oxidation of isoprene. Solid line is seven-point running mean. The equivalent mixing ratio of the condensing vapor (in excess of saturation) can be read off the right axis.

After the lights had been turned off (23:30), the aerosol evaporated continuously at a rate of 17 nm h^{-1}. This corresponds to a mixing ratio in the chamber of 10 pptv below saturation. Therefore 10 pptv is a lower limit for the effective saturation vapor pressure of the condensable products of isoprene.

The running mean of the growth rate (Figure 2) was used to determine the nucleation rate for each measured size bin. The results, grouped together in a statistical plot for clarity, are shown in Figure 3. Each symbol is representative of 300 size bins, tracked backwards in time to their estimated time of nucleation.

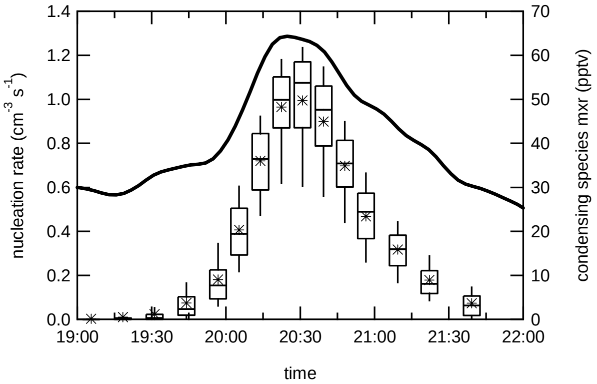

Figure 3. Nucleation rates (average denoted as a double cross; box plot giving 10, 25, 50, 75 and 90 percentile values) determined using PARGAN. Solid line gives the mixing ratio of condensable species (above saturation), proportional to the growth rate.

For an initial mixing ratio of isoprene of 350 ppbv, we found a modest nucleation rate of approximately 1 cm^{-3} s^{-1} (Figure 3), while the condensational growth rate reached a maximum of 100 nm h^{-1} (Figure 2). This suggests that the isoprene oxidation products have a too high saturation vapor pressure to effectively induce nucleation at atmospheric concentrations. However, they probably do contribute to SOA formation in regions where these oxidation products can condense on preexisting aerosol.

The aerosol mass yield (corrected for wall losses; particle density assumed to be 1.4 g cm^{-3}) reached 0.8% at an aerosol volume of close to 4 μm^3 cm^{-3}. This value fits well within the range of measured yields without pre-existing aerosol present (Dommen *et al.*, 2006).

CONCLUSIONS

A nucleation and growth event following isoprene photo-oxidation (initial mixing ratio 350 ppbv) has been analyzed using a novel inverse modelling procedure. Growth rates were found to reach 100 nm h^{-1} while the nucleation rate was relatively low, around 1 cm^{-3} s^{-1}. These empirical rates were determined based on the measured aerosol size distributions, independent of classical nucleation theory. Continuous evaporation after the lights were turned off indicates that 10 pptv is a lower limit of the effective saturation vapor pressure of its condensable oxidation products. The aerosol yield was 0.8%.

Keywords: *Secondary Organic Aerosol, Nucleation, Condensation*

REFERENCES

Dommen J., A. Metzger, J. Duplissy, M. Kalberer, M.R. Alfarra, A. Gascho, E. Weingartner, A.S.H. Prevot, B. Verheggen, and U. Baltensperger, Laboratory observation of oligomers in the aerosol from isoprene/NO_x photooxidation, *Geophys. Res. Lett. 33*, doi: 10.1029/2006GL026523, 2006.

Paulsen, D., J. Dommen, M. Kalberer, A. S. H. Prevot, R. Richter, M. Sax, M. Steinbacher, E. Weingartner, and U. Baltensperger (2005), Secondary organic aerosol formation by irradiation of 1,3,5 –Trimethylbenzene-NO_x-H_2O in a new reaction chamber for atmospheric chemistry and physics, *Environ. Sci. Technol.*, 39, 2668– 2678.

Verheggen, B., and Mozurkewich M. (2006). An inverse modeling procedure to determine particle growth and nucleation rates from measured aerosol size distributions, *Atmos. Chem. Phys.*, *6*, 2927-2942, 2006.

This work was supported by the Swiss national Science Foundation as well as the EC projects EUROCHAMP and POLYSOA.

Indoor Air Nucleation in the Presence of D-limonene

Eija Vartiainen[1,2], Markku Kulmala[1], Kaarle Hämeri[1,2], Taina Ruuskanen[1], Risto Taipale[1] and Hanna Vehkamäki[1]
[1] *Department of Physics, Division of Atmospheric Sciences, P.O.Box 64, 00014,University of Helsinki, Finland*
[2] *Finnish Institute of Occupational Health , Topeliuksenkatu 41 a A, FI-00250, Helsinki, Finland*

INTRODUCTION

Nucleation is a common phenomenon, and despite a great amount of study it is still poorly understood (Kulmala *et al*, 2004). In indoor air nucleation can occur due to oxidation of monoterpenes, such as d-limonene, and then nucleation of the reaction products. Rohr et al., 2003, showed that this reaction has the potential to produce a high number of small particles.

METHODS

We measured particle formation in a room where d-limonene became oxidized. The d-limonene came from orange peeling. Three CPCs with different cut-off sizes (3, 7 and 10 nm) measured particle concentrations. Molecular ion concentrations of the protonated masses 137, 81, 82 and 95 were measured by proton transfer reaction-mass spectrometry. The protonated mass 137 equated to 49 % of the total monoterpene (d-limonene) mass. We also measured the concentration of ozone.

RESULTS

The particle number concentration increased roughly tenfold in five minutes after peeling the orange. Simultaneously the concentration of d-limonene increased to a level of around 100 ppbs' while the concentration of ozone decreased (Figure 1). The particle growth rate, as calculated based on the peaks observed by different CPCs' at 80 seconds, was 6300 nm/h. From this, with a known background concentration, we calculated the concentration of condensable vapour, its source rate, and the nucleation rate, using the method by e.g. Kulmala et al., 2006. The nucleation rate was in the order of 10^5 cm^{-3} s^{-1}.

With both the nucleation rate and the condensable vapour concentration as a function of time, we took logarithms of their values and plotted them against each other. We obtained a linear best fit line (Figure 2). The value of the gradient was proportional to the number of molecules in a critical cluster and the obtained value of 1.2 was in agreement with the activation theory (Kulmala et al., 2006).

DISCUSSION

Indoor air d-limonene oxidation led to nucleation and growth of aerosol particles. Aerosol particle total number concentration increased around tenfold. The results indicate that the primary nucleation mechanism is activation (Kulmala *et al.* 2005).

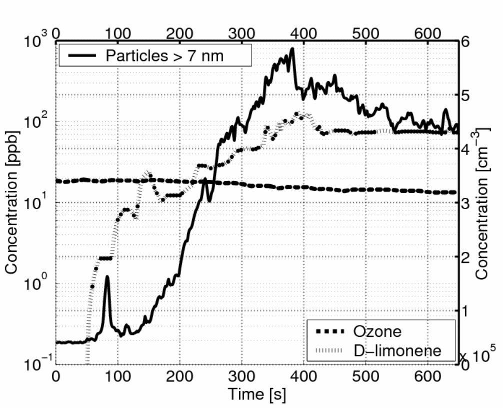

Figure 1. Concentration of aerosol particles (solid line), ozone (dotted line), and d-limonene (dashed line). X-axis shows the time in seconds from the beginning of the experiment.

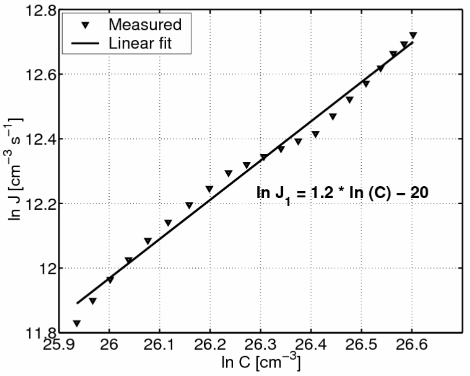

Figure 2. Logarithm of nucleation rate J as a function of logarithm of condensable vapour concentration C and linear fit. The value of the gradient, 1.2, is proportional to the number of the molecules in a critical sized cluster.

Keywords: *Nucleation, Condensation, Indoor aerosols*

REFERENCES

Kulmala, M., Lehtinen, K.E.J. and Laaksonen, A. (2006). *Atmos. Chem. Phys.*, 6, 787-793.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W. and McMurry, P.H. (2004). *J. Aerosol Sci.*, 35, 143-176.

Rohr, A.C., Weschler, C.J., Koutrakis, P. and Spengler, J.D. (2003). *Aerosol Sci. Technol.*, 37, 65-78.

Effect of NH_3 on Nano-particle Formation from SO_2 in Humid Air

Kenkichi Nagato and Tohru Kawabuchi
Department of Mechanical Engineering, Kochi National College of Technology, Nankoku, 783-8508, Japan

INTRODUCTION

The ternary nucleation of H_2SO_4-H_2O-NH_3 has been considered to be one of the key mechanisms of new particle formation in the lower atmosphere (Kulmala *et al.*, 2004). However, the roles of NH_3 molecules in the formation and the growth of nanometer-sized molecular clusters have not been well understood (Yu, 2006). In order to investigate the contribution of NH_3 to the formation and the growth of nano-particles in the atmosphere, we conducted experiments on particle formation by corona discharge in NH_3/SO_2/H_2O/Air mixtures. The size distributions of the nano-particles and the compositions of the ions were measured using the cluster-differential mobility analyzer combined with Faraday cup electrometer (C-DMA/FCE) and the drift tube ion mobility spectrometer/mass spectrometer (DT-IMS/MS), respectively.

EXPERIMENTAL METHODS

The experimental system used in this study consists of a continuous flow gas-generation system, the DT-IMS/MS, and the C-DMA/FCE (Nagato *et al.*, 2005). The NH_3/SO_2/H_2O/Air mixtures were introduced into the corona discharge ionizer. Both ion-induced nucleation and homogenous nucleation are thought to contribute to the particle formation by ionizations in NH_3/SO_2/H_2O/Air mixtures (Kim *et al.*, 1998). In the present measurements, the ions and charged nano-particles generated in the ionization chamber were trapped and only uncharged particles were sent to the C-DMA/FCE for the purpose of investigating the effect of NH_3 on homogenous nucleation.

For ion mass spectrometric measurements, gas mixtures were switched to the DT-IMS/MS, which consists of a drift tube and a quadrupole mass filter. A corona source was mounted in the drift tube.

DMA MEASUREMENTS

The size distributions of the nano-particles generated in SO_2/H_2O/Air mixtures are illustrated by filled symbols in Figures 1(a), 1(b) and 1(c). In a dry air with SO_2 of 1 ppm, the particle formation was very limited. With increasing water vapor concentration to 5000 ppm, a significant formation and growth of nano-particles was observed; the peak of the particle diameter reached 4 nm. Further growth of nano-particles to the diameters of 5-9 nm occurred when the concentration of SO_2 was increased to 50 ppm.

The particle size distributions in the presence of NH_3 (1 ppm) are shown by open symbols. In each condition, the enhancement in particle formation was observed by the addition of NH_3. However, the enhancement factors for particle number concentrations were very small, ranging from 1.2 to 2.2. The average particle diameters were almost unchanged by the

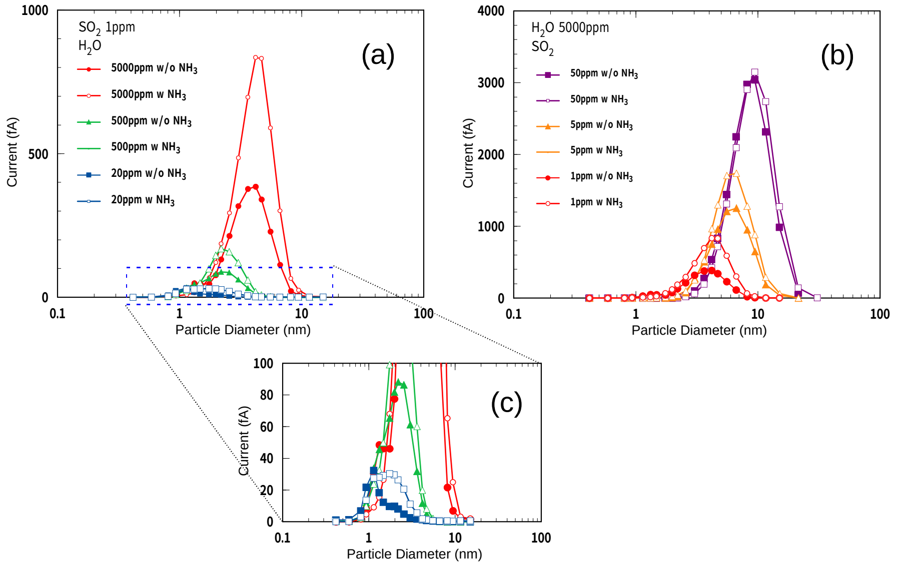

Figure 1. Size distributions of the particles produced by a corona source in SO_2/H_2O/Air (filled symbols) and NH_3/SO_2/H_2O/Air mixtures (open symbols).

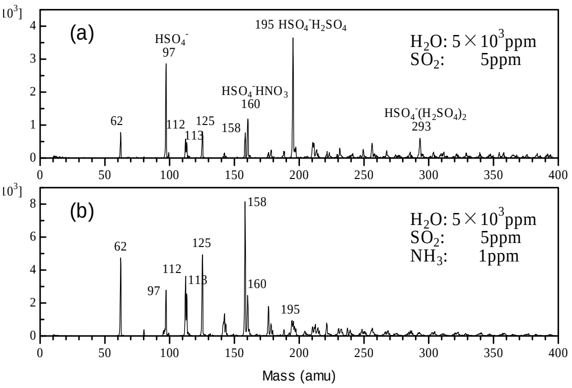

Figure 2. Mass spectra of negative ions in a SO_2/H_2O/Air mixture (a) and a $NH_3/SO_2/H_2O$/Air mixture (b).

addition of NH_3 except for the case of the driest condition.

MASS SPECTROMETRIC MEASUREMENTS

Since a large amount of OH radicals were found to form in humid air by negative corona discharges (Nagato *et al.*, 2006), the formation of H_2SO_4 was expected by corona discharge in humid air containing SO_2. Figure 2(a) shows the mass spectrum of the negative ions generated in a SO_2/H_2O/Air mixture (SO_2: 5 ppm, H_2O: 5×10^3 ppm), in which the ions of $HSO_4^-(H_2SO_4)_n$ (n=0,1,2) dominated. It is therefore confirmed that a significant formation of H_2SO_4 occurred from SO_2 by negative corona discharge. Consequently, nano-particles observed in SO_2/H_2O/Air mixtures were likely formed via binary homogenous nucleation of H_2SO_4-H_2O.

The mass spectrum obtained in a $NH_3/SO_2/H_2O$/Air mixture (NH_3: 1 ppm, SO_2: 5 ppm, H_2O: 5×10^3 ppm) is shown in Figure 2(b), which demonstrates that $HSO_4^-(H_2SO_4)_n$ ions declined significantly by the addition of NH_3. A possible explanation of this change is that H_2SO_4 formed by corona discharge rapidly reacts with NH_3 to form ammonium bisulphate (Anttila *et al.*, 2005), which unlikely participate in ion-molecule reactions. It is also noted that negative ions containing both H_2SO_4 and NH_3 molecules were not observed in the mass spectra. This may imply that NH_3 is less effective in the ion-induced nucleation with $HSO_4^-(H_2SO_4)_n$ ions compared to its contribution to homogenous nucleation with H_2SO_4.

CONCLUSIONS

Nano-particles were observed to form by negative corona discharges in SO_2/H_2O/Air mixtures. The average size of the formed particles increased with the concentrations of H_2O and SO_2. The mass spectrometric measurements confirmed the formation of a large amount of H_2SO_4 from SO_2 particularly in humid air.

The addition of NH_3 enhanced the formation of nano-particles, but the particle number increase only 1.2-2.2 times under the present experimental conditions. In addition, the average particle diameters were almost unchanged, implying that NH_3 has little influence on the growth of nano-particles. The abundance of $HSO_4^-(H_2SO_4)_n$ ions declined by the addition of NH_3, which may suggest the reduction of free H_2SO_4 molecules by the reaction with NH_3.

Keywords: *Ternary nucleation, Ion-induced nucleation, Ammonia*

REFERENCES

Anttila, T., Vehkamäki, H., Napari, I., and Kulmala, M. (2005), Effect of ammonium bisulphate formation on atmospheric water-sulphuric acid-ammonia nucleation, *Boreal Environ. Res.*, 10, 511-523.

Kim, T.O., Ishida, T., Adachi, M., Okuyama, K., and Seinfeld, J.H. (1998). Nanometer-sized particle formation from $NH_3/SO_2/H_2O$/Air mixtures by ionaizing radiation, *Aerosol Sci. Technol.*, 29, 111-125.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.H., (2004). Formation and growth rates of ultrafine atmospheric particles: a review of observation, *J. Aerosol Sci.*, 35, 143-176.

Nagato, K., Matsui, Y., Miyata, T., and Yamauchi, T., (2006). An analysis of the evolution of negative ions produced by a corona ionizer in air, *Int. J. Mass Spectrom.*, 248, 142-147.

Nagato, K., Kim, C.S., Adachi, M., and Okuyama, K. (2005). An experimental study of ion-induced nucleation using a drift tube ion mobility spectrometer/mass spectrometer and a cluster-differential mobility analyzer/Faraday cup electrometer, *J. Aerosol Sci.*, 36, 1036-1049.

Yu, F. (2006). Effect of ammonia on new particle formation: A kinetic H_2SO_4-H_2O-NH_3 nucleation model constrained by laboratory measurements, *J. Geophys. Res.*, 111, D01204, doi:10.1029/2005JD005968.

This work was financially supported by Ministry of Education, Culture, Sports, Science and Technology through Grant-in-Aid for Scientific Research (12480151, 14048227, 16030214).

Growth Rate Analysis of Gas-to-Particle Conversion in Smog Chamber Experiments

Michael Mozurkewich[1], Kristina Zeromskiene[1], and Bart Verheggen[1,2]
[1]*Department of Chemistry and Centre for Atmospheric Chemistry, York University, Toronto, Canada*
[2]*Now at: Institute for Atmospheric and Climate Sciences, ETH, 8092 Zurich, Switzerland*

Smog chambers have been extensively used to investigate the formation of secondary particulate matter as a result of the oxidation of hydrocarbons. Typically these experiments show an increase in yield with time. This is usually interpreted as being due to a shift in gas-particle equilibrium as the amount of organic aerosol matter increases. However, there are other reasons why yield might vary with time. For example, the production of aerosol matter should lag behind the consumption of starting material due to both the non-zero lifetimes of reaction intermediates and the condensation lifetime; the latter might be especially significant if the condensation process is a reaction, such a polymerization. If not accounted for, these cause the yield to increase with time. Also, the condensing species might themselves undergo oxidation. Ignoring these intrinsically time dependent effects can dramatically alter the parameters obtained from an equilibrium model, such as that of Odum et al.(1996).

We are developing an alternative method of analyzing these data. The sequence of size distributions measured during a smog chamber experiment are analyzed using the PARGAN procedure (Verheggen and Mozurkewich, 2006) to obtain the condensational growth rate as a function of time. The procedure corrects for particle wall loss and coagulation. The growth rate provides an indirect measure of the concentrations of the condensing species, offset by their vapor pressures. This quantity is more straightforward to interpret in a kinetic analysis.

Here we report results obtained by applying this method to smog chamber data on the O_3 initiated oxidation of α-pinene and the OH initiated oxidation of β-pinene at high NO.

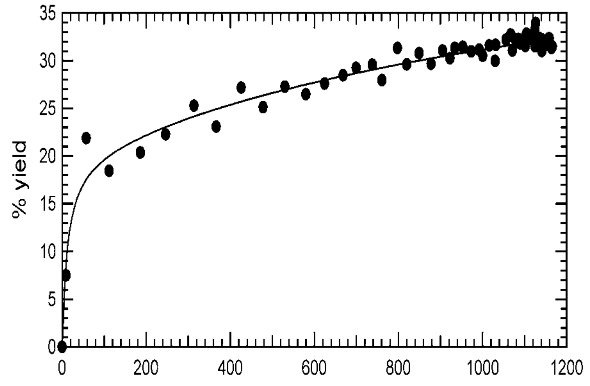

Figure 1. Fit of β-pinene aerosol to a two-component Odum model. Parameters are: K_1 = 0.082 m^3 μg^{-1}, α_1 = 20% and K_2 = 6.4H10^{-4} m^3 μg^{-1}, α_2 = 29%.

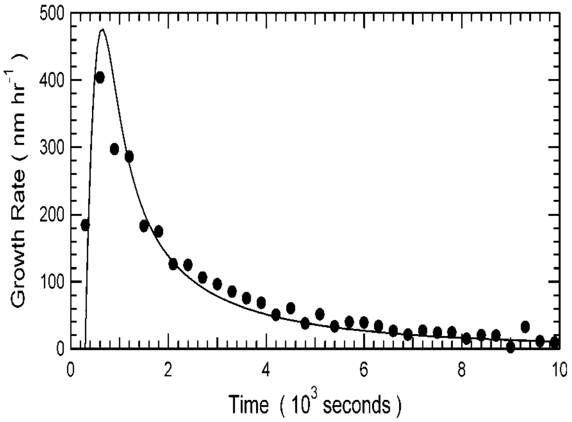

Figure 2. Fit of growth rates derived from the sequence of measured particle size distributions. The fit is for a single condensable product with a yield of 39% and a vapor pressure corresponding to 129 μg m^{-3}.

Figure 1 shows the aerosol yield as a function of organic aerosol mass for the OH induced oxidation of β-pinene. The data are fit well by the Odum et al. model; the fits indicate that there are two semi-volatile components produced with comparable yields. However, Figure 2 shows that the growth rate can be fit quite well with a single condensable component, produced as a product of the initial OH attack. This casts doubt on the reliability of the parameters obtained from the Odum model.

The PARGAN method can also provide nucleation rates. When simultaneous growth rates are available, approximate concentrations of the nucleating species can be obtained, thus giving an estimate of the critical concentration for nucleation.

Keywords: *Gas-to-particle conversion, Smog chamber experiments, Particle growth, Nucleation*

REFERENCES

Odum, J.R., T. Hoffmann, F. Bowman, D. Collins, R.C. Flagan, and J.H. Seinfeld (1996). Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol., 30,* 2580-2585.

Verheggen, B. and M. Mozurkewich (2006). An inverse modeling procedure to determine particle growth and nucleation rates from measured aerosol size distributions, *Atmos. Chem. Phys., 6,* 2927-2942.

Possible Gas Phase Approach to Understanding Tropospheric Nucleation

F. L. Eisele[1,2]
[1] *Atmospheric Chemistry Division, National Center for Atmospheric Research, Colorado, 80303, Boulder, U.S.A.*
[2] *School of Earth and Atmospheric Science, Georgia Institute of Technology, Georgia, 30332, Atlanta, U.S.A.*

The difficulty in understanding tropospheric nucleation is that it is quite likely not a single process but a continuum of chemical processes that vary with local chemistry and RH, where water, ammonia, and other compounds may play competitive roles. In addition, it might also involve very different mechanisms, such as ion induced as opposed to neutral cluster growth. An example of what is being referred to as a continuum of processes, in neutral molecular cluster growth, could be a change in the functional dependence of nucleation on sulfuric acid concentration (and the structure and size of the critical cluster) as ammonia or water concentration is varied. Both compounds can play a similar role of reducing the vapor pressure of sulfuric acid (Marti et al., 1997) and both can change the functional dependence on sulfuric acid nucleation (Ball et al., 1999). If ammonia can enhance the rate of nucleating clusters, then why not larger amines which, though typically present at lower concentrations, can be both more basic as well as less volatile? It is also possible that large organic acids can play the same role as sulfuric acid, or can play this role in conjunction with inorganic acids.

Sulfuric acid is often a focal point because it is unique in a variety of ways. Its relationship to atmospheric particle nucleation is probably more studied and better understood than other potential aerosol precursor compounds, as are the gas phase reactions that lead to its atmospheric production. It is also unique in that it is typically formed from highly volatile compounds, such as SO2, O2, and H2O

$$SO_2 + OH + M \rightarrow HSO_3 + M$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2$$

$$SO_3 + H_2O \underset{\text{in water}}{\overset{\text{nonlinear}}{\rightarrow}} H_2SO_4$$

but ends up super saturated, even at its typically sub pptv atmospheric concentrations. Since most nucleation events appear to occur during sunlight hours, it is quite possible that photochemical oxidation plays a role in generating most nucleation precursors, probably by reactions that add functional groups which reduce volatility. It is, however, hard to think of any that could come close to the change in vapor pressure between SO2 and H2SO4. Plants also have emission rates that are sunlight dependent, but can plants directly emit compounds into the atmosphere that are supersaturated? If so, how long will they stay supersaturated, and does nearly all the resulting nucleation occur near the plant leaf?

This suggests using gas phase measurements to help identify nucleation precursors by looking for direct biogenic emissions or their oxidation products that are at concentrations close to their saturation limit. While these concentration limits are poorly known they could be studied in the laboratory. Another possibility is to look for compounds whose concentration falls rapidly, due to condensation, when their sunlight source is turned off. Ultimately, it is going to be fairly difficult to clearly identify compounds other than sulfuric acid that might initiate nucleation without the use of supporting laboratory gas phase studies which define which specific compound can self nucleate or that can nucleate in conjunction with other specific compounds at ambient concentrations. A big part of understanding non-sulfate nucleation is first to be able to identify it. Since as few as two or maybe even one sulfuric acid molecule may be responsible for initiating nucleation, particles/clusters must be found to contain no sulfuric acid in order to show, by direct chemical measurement, that sulfuric acid is not involved in a specific nucleation event,. Assuming ambient daytime concentrations of sulfuric acid are in the 106-107 molecules cm-3 concentrations range with a reaction rate coefficient on the order of 10-9 cm3 molecules-1 s-1, even a particle that nucleates independent of sulfur acid may acquire a sulfuric acid molecule after about 102 s. After non-sulfate nucleation has been identified, potential precursors that appear to be involved must be studied in the laboratory to determine their nucleating potential under the environment conditions in which they are found and quantitatively observed in the field. To identify these precursors, measurements and correlation plots will be needed for both the compounds found on the smallest, most recently nucleated particles and of the largest, stickiest, and most difficult to measure gases. Not an easy task.

Many of these same problems exist for ion induced nucleation, though differences in ion polarity should make separating out sulfate driven nucleation easier. Also, particularly in the mid to upper troposphere, there is no rule that says that ion and neutral cluster growth are not fully intertwined with ion recombination products forming a core for neutral critical clusters and ion charging helping to increase the growth rate of clusters that were initially neutral.

REFERENCES

Marti, J., A. Jefferson, X. Cai, C. Richert, P. McMurry and F. Eisele, 1997: H_2SO_4 vapor pressure of sulfuric acid and ammonium sulfate solutions. JGR, 102, 3725-3735.

Ball, S., D. Hanson and F. Eisele, 1999: Laboratory studies of particle nucleation: Initial results for H2SO4, H2O, and NH3 vapors. JGR, 104, 23,709-23,718.

Effect of formic acid, acetic acid and ammonia on stability of sulfuric acid–water complexes

A. B.Nadykto[1*] **and F.Yu**[1]
[1]*State University of New York at Albany, ASRC, 251 Fuller Rd., Albany 12203, NY, USA*

INTRODUCTION

Reliability of DFT and ab initio methods in predicting the structure and properties of ionic clusters is well known. Neutral H_2SO_4-H_2O and H_2SO_4-H_2O-NH_3 clusters have also been studied using DFT B3LYP in the past. However, comparison of DFT B3LYP predictions (Re et al., 2000; Ianni and Bandy, 1998; 1999) with experiments (Hanson and Eisle, 2000) shows obvious discrepancies. These deviations have been attributed by Vehkamaki et al. (2004) to "insufficient accuracy of ab initio calculations". Here the effect of ammonia on the formation of sulfuric acid-water cluster is studied using a more accurate method. We also investigate the effect of common organic acids such as formic and acetic acids on thermodynamic stability of sulfuric acid-water complexes.

METHODS

Our tests lead us to conclude that results given by B3LYP should be reassessed using a more accurate method. PW91 is likely a good alternative. Our results (Nadykto et al, 2006a) are consistent with findings of Tsuzuki and Luthi (2001), who pointed out serious problems of the widely used B3LYP in predicting intermolecular interactions, and showed moderate computational costs, weak basis set dependency, and good overall performance of PW91, close to that of MP2, making DFT PW91 a viable alternative to the higher level MP2 method. In this paper, hydrogen bonded of sulfuric acid with water, ammonia, formic acid and acetic acid are studied using Density Functional Theory (DFT) at PW91PW91/6-311++G(3df,3pd) level.

RESULTS AND DISCUSSION

We found that changes in the Gibbs free energy associated with mono-, di- and tri-hydration obtained in our study (Nadykto and Yu, 2006b) are ~2–4 kcal mole^{-1} more negative than those obtained using B3LYP. Our results are consistent with experimental data. The hydration energy of the H_2SO_4 dimer increases with the number of water molecules in the cluster for m=0-3. Our results show that the Gibbs free energy of the $NH_3 + H_2SO_4 = NH_3 (H_2SO_4)$ reaction (-7.77 kcal mole^{-1}) is 3.2 kcal mole^{-1} more negative than that given by Ianni and Bandy (2000). Our calculations indicate that NH_3 (H_2SO_4) cluster is about 2.1 kcal mole^{-1} more stable than a dimer of H_2SO_4 (-5.68 kcal mole^{-1}). We did not observe any enhancement in the affinity of water to NH_3 $(H_2SO_4)_n(H_2O)_m$ compared to $(H_2SO_4)_n(H_2O)_m$. In fact, the affinity of water to NH_3 $(H_2SO_4)_n(H_2O)_m$ is a bit lower than that to $(H_2SO_4)_n(H_2O)_m$. However, our preliminary calculations indicate that Gibbs free energies for reactions of ammonia with hydrated H_2SO_4 dimers are higher than those with hydrated H_2SO_4 monomers. This may be an indication that the efficiency of ammonia as a stabilizer of H_2SO_4-water clusters grows with cluster size.

We have also investigated the effect of formic and acetic acids on the thermodynamic stability of binary sulfuric acid-water clusters. It has been found that sulfuric acid forms thermodynamically stable complexes with formic and acetic acids. Stabilizing effect of these organic acids is either close to or exceeds that of ammonia, which is a commonly accepted principal stabilizer of H_2SO_4-H_2O clusters in the atmosphere. In addition to strong hydrogen bonding with sulfuric acid, both formic and acetic acids can form thermodynamically stable clusters with water and ammonia. This leads us to conclude that these common organic substances can efficiently stabilize small sulfuric acid-water clusters and their involvement, alongside with or without ammonia, in the atmospheric nucleation should be studied in details further.

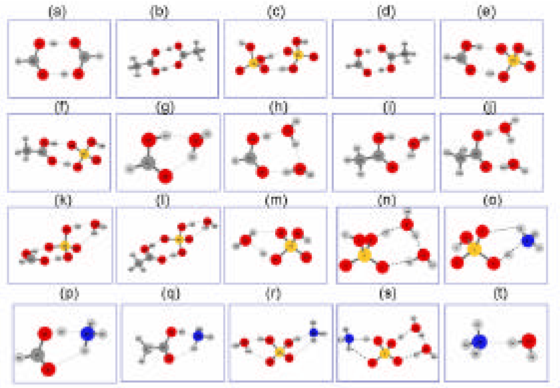

Fig.1. Equilibrium geometries of most stable isomers calculated using DFT at PW91PW91/6-311++G(3df,3pd) level: (a) $(CH_2O_2)_2$; (b) $(C_2H_4O_2)_2$; (c) $(H_2SO_4)_2$; (d) $(CH_2O_2)(C_2H_4O_2)$; (e) $(CH_2O_2)(H_2SO_4)$; (f) $(C_2H_4O_2)(H_2SO_4)$; (g) $(CH_2O_2)(H_2O)$; (h) $(CH_2O_2)(H_2O)_2$; (i) $(C_2H_4O_2)(H_2O)$; (j) $(CH_2O_2)(H_2O)$; (k) $(CH_2O_2)(H_2SO_4)(H_2O)$; (l) $(C_2H_4O_2)(H_2O)$; (m) $(H_2SO_4)(H_2O)$; (n) $(H_2SO_4)(H_2O)_2$; (o) $(H_2SO_4)(NH_3)$; (p) $(CH_2O_2)(NH_3)$; (q)$(C_2H_4O_2)(NH_3)$; (r) $(H_2SO_4)(H_2O)(NH_3)$; (s) $(H_2SO_4)(H_2O)_2(NH_3)$; and (t) $(H_2O)(NH_3)$.

Optimized geometries and thermochemical properties of formic acid-sulfuric acid-water clusters and acetic acid–sulfuric acid-water clusters (Nadykto and Yu, 2006a) are given in Fig.1 and Table 1, respectively.

Optimized geometries and thermochemical properties of $NH_3(H_2SO_4)_n(H_2O)_m$ clusters (Nadykto and Yu, 2006b) are given in Fig.2 and Table 2, respectively.

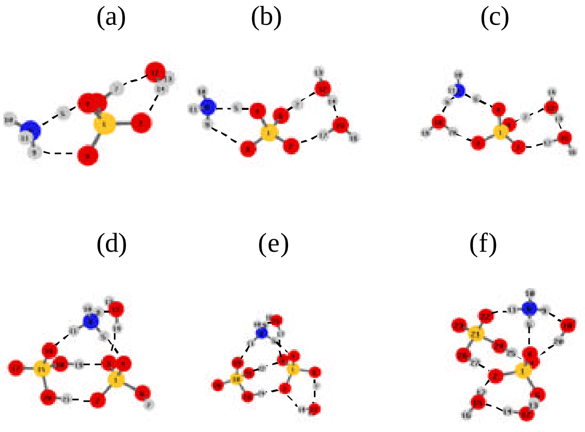

Fig.2. Equilibrium geometries of most stable isomers calculated using DFT at PW91PW91/6-311++G(3df,3pd) level: (a) $(H_2SO_4)(H_2O)(NH_3)$; (b) $(H_2SO_4)(H_2O)_2(NH_3)$;(c) $(H_2SO_4)(H_2O)_3(NH_3)$; (d) $(H_2SO_4)_2(H_2O)$ (NH_3); (e) $(H_2SO_4)_2(H_2O)_2(NH_3)$; (f) $(H_2SO_4)(H_2O)_3(NH_3)$.

Table1. Gibbs free energy changes (kcal mole $^{-1}$) associated with reactions among clusters composed of sulfuric acid (S), water (W), acetic acid (C) and formic acid (F) and at T=298.15K and P=101.3 KPa.

S+F=SF	-6.44	S+FW=SFW	-8.36
S+C=SC	-7.46	S+CW=SCW	-9.4
C+C=C_2	-6.26	SW+ F=SFW	-6.53
F+F=F_2	-5.69	SW+C=SCW	-7.64

Table2. Gibbs free energy changes (kcal mole $^{-1}$) associated with reactions among clusters composed of sulfuric acid (S), water (W), and ammonia (A) at T=298.15K and P=101.3 KPa.

S+S=S_2	-5.59	SA+W=SAW	-1.52
SA+S=S_2A	-11.65	SAW+W=SAW_2	-2.31
SAW+S=S_2AW	-12.59	SAW_2+W=SAW_3	-1.21
SW_3+S=S_2W_3	-4.45	SW+A=SAW	-6.90
S+A=SA	-7.77	SW_2+A=SAW_2	-6.18

Keywords: *Binary Clusters, Ternary Clusters, Gibbs Free Energy, Thermodynamic Stability, Sulfuric Acid-Water-Organic Acid Complexes, DFT.*

REFERENCES

Bandy, A. R. and J. C. Ianni (1998), Study of the Hydrates of H_2SO_4 Using Density Functional Theory, *J. Phys. Chem. A*, *102*(32), 6533.

Hanson, D. R., and F. L. Eisele (2000), Diffusion of H_2SO_4 on humidified nitrogen: Hydrated H_2SO_4, *J. Phys. Chem. A*, *104*, 1715.

Nadykto A.B., and F. Yu (2006a), Strong hydrogen bonding between atmospheric nucleation precursors and common organics, Chem. Phys. Lett., revised.

Nadykto A.B., and F. Yu (2006b), Stabilizing effect of ammonia on clustering of atmospheric nucleation precursors, *J. Phys. Chem B.*, revised.

Re, S., Y. Osamura, and K. Morokuma (1999), Coexistence of neutral and ion-pair clusters of hydrated sulfuric acid $H_2SO_4(H2O)_n$ (n = 1 - 5)—A molecular orbital study, *J. Phys. Chem. A*, *103*, 3535

Tsuzuki, S. and H.P. Luthi (2001), Interaction energies of van der Waals and hydrogen bonded systems calculated using density functional theory: Assessing the PW91 model. J. *Chem. Phys.*, *114*, 3949.

Vehkamäki, H., I. Napari, M. Kulmala, and M. Noppel (2004), Stable Ammonium Bisulfate Clusters in the Atmosphere, *Phys. Rev. Lett.*, *93*, 148501.

This work was supported by US National Science Foundation.

The role of competitive dynamic condensation and evaporation of NH_3, HNO_3, and HCl in the growth of freshly nucleated sulfuric acid particles

Rahul A. Zaveri and Richard C. Easter
Pacific Northwest National Laboratory, Richland, WA 99352, USA

INTRODUCTION

Condensation and evaporation of trace gases on freshly nucleated sulfuric acid particles play an important role in their subsequent growth. While sulfuric acid is usually treated as a non-volatile species, the characteristic times for reversible condensation and evaporation of semi-volatile gases such as HNO_3, HCl, and NH_3 can vary widely between aerosol particles of different sizes, sometimes by several orders of magnitude. For example, fine mode particles may reach equilibrium in a few seconds while coarse mode particles may take several hours. Thus, the system of coupled ordinary differential equations (ODEs) that describes mass transfer between gases and particles of different sizes is extremely stiff, and hence computationally expensive to solve.

To overcome this problem, hybrid solution techniques are often used in which all the fine mode particles (less than 1 μm) are assumed to be in bulk equilibrium with the gas-phase while a dynamic solution is used for the coarse mode (*Capaldo et al.*, 2000). In this paper, we examine the role of competitive dynamic condensation and evaporation of HNO_3, HCl, and NH_3 in the growth of freshly nucleated sulfuric acid particles. We also evaluate an alternative, computationally efficient approach for solving the fully dynamic system for aerosols of all sizes.

APPROACH

For a given aerosol size section, condensation and evaporation of semi-volatile gases such as HNO_3, HCl, and NH_3 depend on their equilibrium surface vapor concentrations, particle diameter (for diffusion limitation and Kelvin effect) and surface area. The bulk equilibrium assumption for all the fine mode particles used in hybrid techniques cannot resolve the effects of compositional and phase state differences on the driving forces and growth rates of different modes. Thus, while the hybrid approach may yield satisfactory results for the overall fine mode equilibrium aerosol mass, it tends to introduce errors in the growth rates of particles of different compositions and sizes. This is especially important in the growth of freshly nucleated sulfuric acid particles which have high surface area but very little mass compared to the accumulation mode.

Here, we first investigate the effect of size-resolved composition and phase state on the competitive growth of freshly nucleated sulfuric acid particles and larger fine mode aerosols using a rigorous, fully dynamic mass transfer solver coupled with a comprehensive thermodynamic module (*Zaveri et al.*, 2005a,b). We will then discuss the development and evaluation of a new algorithm called ASTEEM (Adaptive-step Species Time-split Explicit Euler Method) that overcomes the computational challenges in the rigorous technique.

ASTEEM first solves the condensation of non-volatile H_2SO_4 and semi-volatile NH_3 for all the aerosol sections simultaneously over the host 3-D model time-step (usually ~5 min). It then solves the coupled condensation/evaporation of HNO_3, HCl, and NH_3 gases for each size section in a time-split fashion over a chosen time-splitting interval (TSI). The value of TSI is estimated such that the maximum overall change in the gas-phase concentrations of the semi-volatile species over the interval is less than ~10% (or a user-specified value). This approach significantly reduces the stiffness of the system, thus allowing the solver to take much longer time steps than are required when all the species in all the sections are integrated simultaneously.

CONCLUSIONS

Model analysis shows that competitive dynamic exchange of NH_3, HNO_3, and HCl over aerosols of different compositions and sizes play an important role in their subsequent growth. Bulk equilibrium and hybrid solution approaches may simulate overall bulk mass well but can introduce errors in the number size distribution of fine mode aerosols. A dynamic yet computationally efficient technique is presented.

Keywords: *Dynamic gas-particle partitioning, aerosol modeling, aerosol thermodynamics, aerosol growth*

REFERENCES

Capaldo K.P., C. Pilinis, and S.N. Pandis (2000). A computationally efficient hybrid approach for dynamic gas/aerosol transfer in air quality models, *Atmos. Environ*., 34, 3617-3627.

Zaveri R. A., Easter R. C., and Wexler A. S (2005a). A new method for multicomponent activity coefficients of electrolytes in aqueous atmospheric aerosols, *J. Geophys. Res.*, 110, D02201, doi:10.1029/2004JD004681.

Zaveri R. A., Easter R. C., and Peters L. K. (2005b). A computationally efficient multicomponent equilibrium solver for aerosols (MESA), *J. Geophys. Res.*, 110, D24203, doi:10.1029/2004JD005618..

Cluster Non-Accommodation: Barriers to Small Cluster Growth and Their Effect on Atmospheric Particle Size Distributions

Chongai Kuang[1], Peter H. McMurry[2], Alon V. McCormick[1], and Michael R. Zachariah[3]
[1]Department of Chemical Engineering & Materials Science, University of Minnesota, 55455, Minneapolis, USA
[2]Department of Mechanical Engineering, University of Minnesota, 55455, Minneapolis USA
[3]Department of Mechanical Engineering, University of Maryland, 20742, College Park, USA

INTRODUCTION

Atmospheric measurements carried out over the past decade have shown that new particles are often formed by nucleation from the gas phase. The widespread occurrence of frequent nucleation events and the rapid growth of nucleated particles suggest that nucleation may play an important role in determining the concentration of cloud condensation nuclei and the resultant extent of cloud cover (Laaksonen *et. al.*, 2005). The relationship between nucleation and cloud cover needs to be understood in order to establish reliable global climate models.

While much has been learned about nucleation over the past decade, it is not yet possible to predict, *a priori*, rates at which particles are formed and grow. Atmospheric aerosol measurements made in Atlanta during the summer of 2002 illustrate the inadequacy of the current understanding of particle formation (McMurry *et. al.*, 2005). In Figure 1, typical results from that study are shown where the measured particle size distributions were one to two orders of magnitude below the prediction from collision-controlled theory, which treats nucleation as a coagulation-limited process where every particle-particle collision is effective (McMurry, 1983). This suggests that collision-controlled theory overestimates rates of particle production.

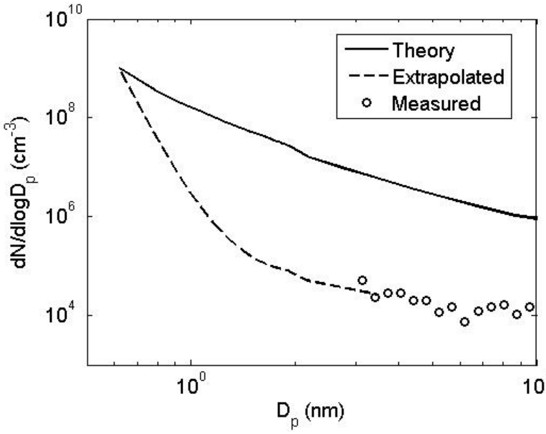

Figure 1. Comparison of aerosol size distribution measured on 8/19/02 in Atlanta, Georgia (McMurry *et. al.*, 2005), with the prediction from collision-controlled theory. Included is the measured size distribution extrapolated from the lower limit of particle size detection (~ 3 nm) to the measured monomer concentration.

Collision-controlled theory assumes that cluster growth rates are given by the monomer collision frequency multiplied by an accommodation coefficient usually set to unity (McMurry, 1983). This accommodation coefficient describes the probability that upon collision, a monomer "sticks" to a cluster resulting in the formation of a stable product cluster. Conversely, non-accommodation describes monomer-cluster collisions that do not result in stable product clusters.

The discrepancy in Figure 1 between measured and predicted size distributions is believed to occur due to barriers of formation for the smallest molecular clusters; they are formed at rates well below their collision frequency.

This work incorporates the effects of cluster non-accommodation into an aerosol growth model and simulates nucleation events measured at three urban sites: (1) Atlanta, Georgia in the summer of 2002 (McMurry *et. al.*, 2005), (2) Boulder, Colorado in the fall of 2004 (Eisele *et. al.*, 2006), and (3) Mexico City, Mexico in the spring of 2006.

CLUSTER NON-ACCOMMODATION

This barrier to small cluster formation can be understood within the context of bimolecular reaction rate theory, where a monomer-cluster collision forms an energized cluster complex that can either decay back to reactants or be stabilized by collision with a third body (Holbrook *et. al.*, 1996). The lifetime of the cluster complex is inversely related to its size, since the ability of a cluster to accommodate collision energy is dependent on its number of internal degrees of freedom (Holbrook *et. al.*, 1996). Energized clusters with short lifetimes would decay before they could be stabilized to form product clusters, resulting in a small accommodation coefficient. The accommodation coefficient is therefore believed to be small for monomer-monomer collisions and to asymptotically approach unity for collisions between monomers and large clusters as shown in Figure 2. It is believed that this competition between decay and stabilization is a key interaction that limits cluster growth in the small size regime.

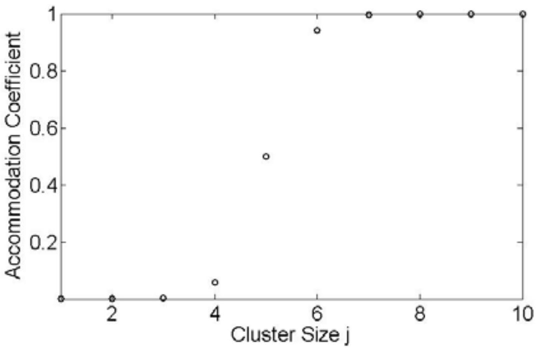

Figure 2. Accommodation coefficient for collisions between monomers and clusters of size *j*.

THEORY

The time evolution of the aerosol size distribution is simulated using a discrete-sectional approach (Rao and McMurry, 1989). The cluster population balance equations include terms that describe monomer condensation on clusters and pre-existing aerosol, coagulation between clusters, coagulation between clusters and pre-existing aerosol, and a constant rate of monomer production. The effects of cluster non-accommodation are incorporated into the growth model by multiplying each collision kernel with the corresponding accommodation coefficient.

A functional form for the cluster accommodation coefficient is used that depends on two parameters: the monomer-monomer accommodation coefficient, P_{11}, and the cluster size at which the accommodation coefficient is unity, x_{max}. These two quantities are used as best-fit parameters when optimizing the simulated and measured particle size distributions.

Several assumptions are made in this numerical study: the condensing monomers are sulphuric acid molecules, particle growth rates are limited by sulphuric acid condensation rates, and the growing particles consist primarily of ammonium and sulphate (Sakurai *et. al.*, 2005).

RESULTS AND DISCUSSION

A typical best-fit simulation result is shown in the upper panel of Figure 3, where the data is plotted as a contour of particle size distribution versus time, with the corresponding measured size distribution in the lower panel. The measured particle size distribution in Figure 3 is typical of the nucleation events analyzed in this study where there is a discernable nucleation mode exhibiting steady growth for an hour or more.

The parameters P_{11} and x_{max} were optimized by minimizing the sum of residuals over particle size and time. The simulated and measured distributions are in qualitative agreement and suggest that incorporating the effects of cluster non-accommodation can allow for a more accurate prediction of measured size distributions.

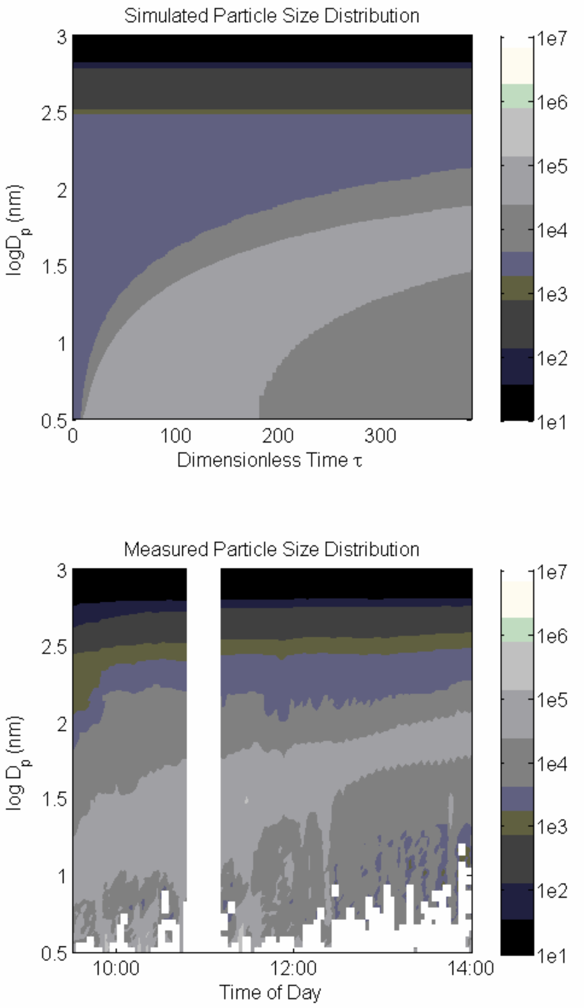

Figure 3. A comparison of an aerosol size distribution measured on 8/05/02 in Atlanta, Georgia (McMurry *et. al.*, 2005) with the best-fit simulation result where $P_{11} = 9 \times 10^{-3}$ and $x_{max} = 10$. The contour plot indicates the particle number distribution function in units of cm^{-3}.

A similar analysis was performed for 8 more nucleation events spanning the Atlanta, Boulder, and Mexico City sampling sites. The corresponding best-fit values of P_{11} and x_{max} for each nucleation event are shown in Figure 4. The optimized values of P_{11} for each x_{max} are all within an order of magnitude of each other over all the analyzed nucleation events. This similarity in sensitivity over such various nucleation sites suggests that cluster non-accommodation is inherent to the particle growth process in the small size regime.

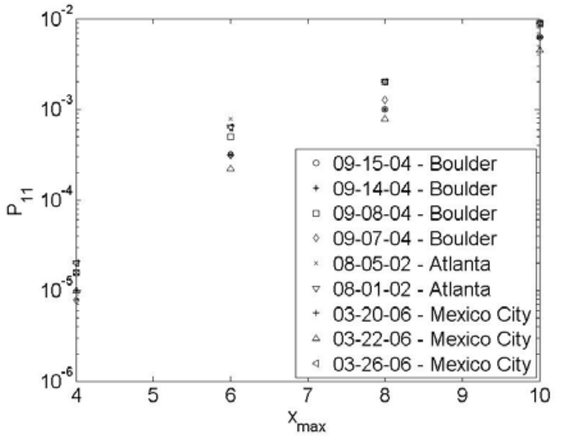

Figure 4. Best-fit values of P_{11} and x_{max} for various nucleation events in Boulder, CO, Atlanta, GA, and Mexico City, Mexico.

CONCLUSION

Numerical simulations were performed to model the time and particle size evolution of an atmospheric aerosol incorporating the effects of cluster non-accommodation. The simulated results qualitatively predict the measured size distributions for various nucleation events at different times and locations, suggesting the importance of cluster non-accommodation in the growth of small particles.

Keywords: *Cluster Non-Accommodation, Atmospheric Nucleation, Discrete-sectional Method*

REFERENCES

Eisele, F. L., E. R. Lovejoy, E. Kosciuch, K. F. Moore, R. L. Mauldin III, J. N. Smith, P. H. McMurry, and K. Iida (2006). Negative atmospheric ions and their potential role in ion-induced nucleation, *J. Geophys. Res.*, *111*, D04305, doi:10.1029/2005JD006568.

Friedlander, S., Lai, F., Hidy, G. and Pich, J. (1972). The self-preserving particle size distribution for Brownian coagulation in the free-molecule regime. *Journal of Colloid and Interface Science* **39** [No. 2] 395 – 405.

Holbrook, K., Pilling, M. and Robertson, S. (1996). *Unimolecular Reactions*. 2nd edition Wiley & Sons, New York.

Laaksonen, A., A. Hamed, J. Joutsensaari, L. Hiltunen, F. Cavalli, W. Junkermann, A. Asmi, S. Fuzzi, and M. C. Facchini (2005). Cloud condensation nucleus production from nucleation events at a highly polluted region. *Geophys. Res. Lett.*, 32, L06812, doi:10.1029/2004GL022092.

McMurry, P. H. (1983). New particle formation in the presence of an aerosol: Rates, time scales, and sub-0.01 μm size distributions, *Journal of Colloid and Interface Science* **95** [No. 1] 72 – 80.

McMurry, P. H., M. Fink, H. Sakurai, M. R. Stolzenburg, R. L. Mauldin III, J. Smith, F. Eisele, K. Moore, S. Sjostedt, D. Tanner, L. G. Huey, J. B. Nowak, E. Edgerton, and D. Voisin (2005). A criterion for new particle formation in the sulfur-rich Atlanta atmosphere. *J. Geophys. Res.*, *110*, D22S02, doi:10.1029/2005JD005901.

Rao, N. and McMurry, P. H. (1989). Nucleation and growth of aerosol in chemically reacting systems. A theoretical study of the near-collision-controlled regime. *Aerosol Science and Technology*, **11** [No. 2] 120 – 132.

Sakurai, H., M. A. Fink, P. H. McMurry, L. Mauldin, K. F. Moore, J. N. Smith, and F. L. Eisele (2005). Hygroscopicity and volatility of 4–10 nm particles during summertime atmospheric nucleation events in urban Atlanta. *J. Geophys. Res.*, *110*, D22S04, doi:10.1029/2005JD005918.

This work was supported primarily by the IGERT Program of the National Science Foundation under Award Number DGE-0114372.

Statistical Mechanics of Aqueous Sulfuric Acid and Ionic Clusters

Shawn M. Kathmann, Gregory K. Schenter, Bruce C. Garrett
Molecular Interactions and Transformations Group, Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, 99352

INTRODUCTION

Understanding the chemical physics of small molecular clusters is central to describe the nature of nucleation. Nucleation depends on the molecular cluster thermodynamics and kinetics. The cluster partition function serves as the bridge between the molecular interaction potentials and cluster thermo-kinetic properties. Once these properties are known at the appropriate conditions the nucleation rate can be predicted. Our work (Kathmann *et al.*, 2002) has shown that the sensitivity of nucleation is due to the delicate balance of interaction strengths, zero-point-energy (ZPE), and statistical mechanical sampling. For example, tenths of a kcal/mol variation in the free energy differences can alter the nucleation rate by many orders of magnitude. These small variations can arise from uncertainties in the interaction energies, ZPE, or inadequate sampling of configuration space.

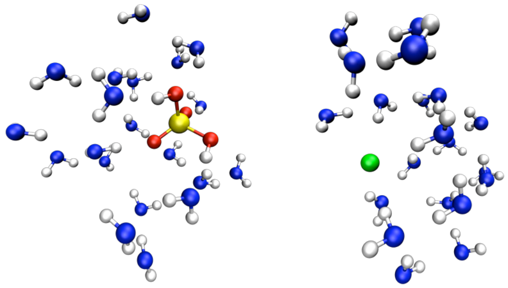

Figure 1. Aqueous clusters of H_2SO_4 and Cl-.

Dynamical Nucleation Theory (DNT) (Schenter *et al.*, 1999; Kathmann *et al.*, 1999 and 2002) is a molecular-level treatment of nucleation kinetics based upon variational transition state theory to obtain rates and free energies for the underlying clustering reactions. Thus, DNT requires accurate interaction energies as well as statistical mechanical sampling of thermally relevant regions of cluster configuration space. The classical cluster Helmholtz free energy A_i is related to the partition function Q_{DNT} via

$$e^{-\beta A_i} = Q_{DNT} = \int_v d\mathbf{r}^i \exp\left[-\beta U\left(\mathbf{r}^i\right)\right]\chi(v) \qquad (1)$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant, T is the temperature, $U(\mathbf{r}^i)$ is the interaction potential, and $\chi(v)$ is a characteristic function defining the relevant volume of configuration space.

The presence of trace components (e.g., H_2SO_4 or ions – see Figure 1) can reduce the pure H_2O nucleation barrier due to the enhanced stabilization between cluster species. We have performed accurate *ab initio* calculations (MP2/aug-cc-pvdz) on aqueous H_2SO_4 clusters to parameterize H_2SO_4-H_2O interaction potentials such that ZPE was implicitly included by fitting the binding energy so that it matched the ZPE corrected *ab initio* binding energy. Figure 2 shows the calculated (from Eq. 1) anharmonic cluster Helmholtz free energy differences (which are equivalent to the size-dependent chemical potentials = $\mu_{i,i-1}$) between adjacent-sized H_2SO_4 hydrates parameterized with and without ZPE compared to those for pure H_2O. Clearly, inclusion of ZPE in the chemical potentials for H_2SO_4 hydrates can cause discrepancies ranging from ~1.8 down to 0.2 kcal/mol. Also, the H_2SO_4 hydrate $\mu_{i,i-1}$ are lower than $(H_2O)_i$ for hydrates with two or fewer waters, however, for the tri-hydrate and larger the $\mu_{i,i-1}$ are less stable because the proton transfer, $H_2SO_4\left(H_2O\right)_i \leftrightarrow HSO_4^- \cdot H_3O^+\left(H_2O\right)_{i-1}$, was neglected. The proton transfer step becomes more probable when H_2SO_4 is surrounded by 3 or 4 H_2O and will become more stable than the pure water clusters.

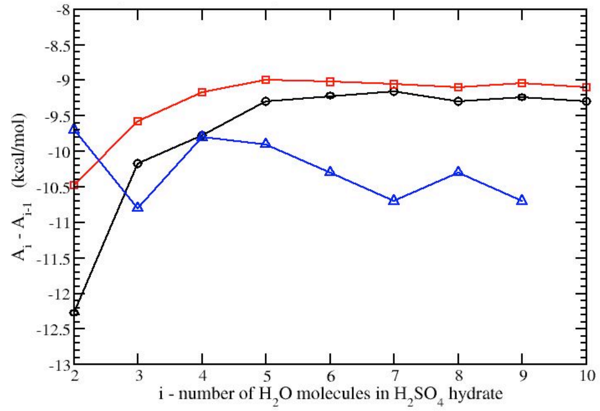

Figure 2. $H_2SO_4(H_2O)_i$ hydrate anharmonic chemical potentials with (red squares) and without ZPE (black circles) compared to pure TIP4P water (blue triangles) chemical potentials at 298K.

We now consider the influence of anharmonicity on the chemical potentials using pure H_2O clusters. Here we use the Dang-Chang polarizable potential for water at 243K. We compare the chemical potentials using the Rigid-Rotor Harmonic Oscillator Approximation (RRHOA) which uses the energetic minima to the full anharmonic statistical sampling using 10's to 100's of millions of configurations – see Figure 3. This comparison shows that using the RRHOA without quantifying its effect is unjustified.

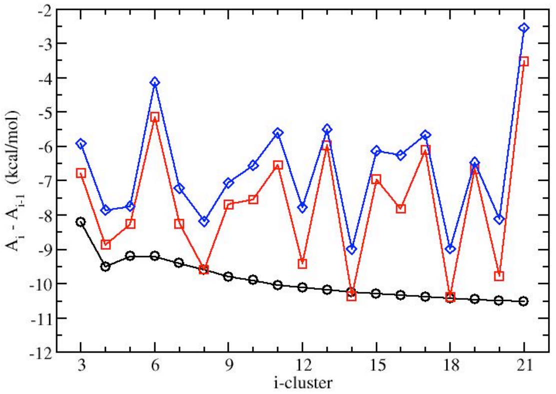

Figure 3. Size-dependent chemical potential for fully anharmonic chemical potentials (black circles) compared to the RRHOA quantum (blue diamonds) and classical (red squares) results at 243K. The difference between the quantum and classical RRHOA results from the ZPE.

We have also studied (Kathmann *et al.*, 2005) the breakdown of the Classical Ion-Induced Nucleation Theory (CNT) when compared to a statistical mechanical treatment of aqueous ionic clusters. The size-dependent anharmonic chemical potentials of aqueous ionic clusters using ions of different Lennard-Jones size (σ_{Na} = 2.35Å and σ_{Cl} = 4.40Å) and sign (+/-) are shown in Figure 4: red circle (- and 2.35Å), yellow diamond (+ and 2.35Å), green triangle up (- and 4.40Å), blue triangle down (+ and 4.40Å), purple square (pure TIP4P water), upper dotted (CNT w/ion radius = 0.1Å), lower dotted (CNT w/ion radius = 10 Å), solid black (CNT pure water).

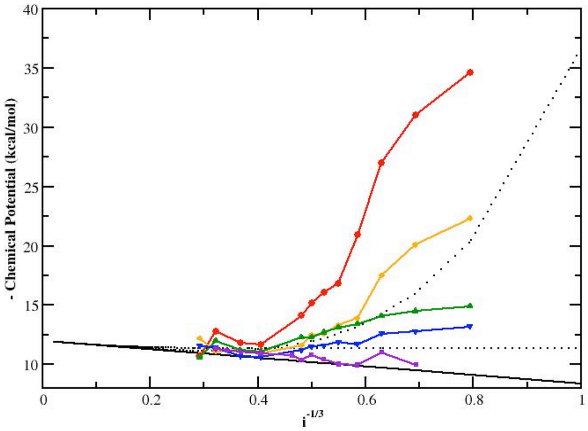

Figure 4. Size-dependent chemical potential for +/- ions of different Lennard-Jones size parameters compared to the CNT results for aqueous ionic and pure water clusters at 243K.

The small (+) and large (–) ion interactions correspond to Na+ and Cl-, respectively. One can see from Figure 4 that CNT does not provide the correct trend quantitatively or qualitatively.

CONCLUSIONS

Given the extreme sensitivity of nucleation to cluster interaction potentials, ZPE, and statistical mechanical sampling emphasis should be placed on improving all three aspects. DNT utilizes these aspects of chemical physics to obtain accurate cluster kinetics and thermodynamics.

CNT, although offering insight into the some aspects of nucleation, has outlived it's quantitative utility and should be modified or replaced by modern developments in cluster chemical physics.

Our analysis has shown that using the RRHOA chemical potentials (i.e., using a single energetically favorable minima) may cause the greatest errors when calculating and predicting aqueous cluster thermodynamics, kinetics, and mechanisms. This can be remedied by sampling more of the cluster configuration space albeit at the expense of greater computational effort because so many energy evaluations are needed to construct the appropriate thermal ensemble.

The next area to focus attention on is the construction of interaction potentials from high quality electronic structure calculations with ZPE either implicitly (as we did for the H_2SO_4 hydrates) or explicitly included. Once these key ingredients are shown to be sufficiently accurate quantitative prediction of absolute nucleation rates will become possible.

Keywords: Interaction potentials, sensitivity, cluster free energies, anharmonicity

REFERENCES

1. Schenter, G.K., Kathmann S.M., and Garrett, B.C., (1999), *Phys. Rev. Lett.*, **82**, 3484.
2. Schenter, G.K., Kathmann, S.M., and Garrett, B.C., (1999), *J. Chem. Phys.*, J. Chem. Phys., **110**, 7951.
3.Kathmann, S.M., Schenter, G.K., and Garrett, B.C., (1999) *J. Chem. Phys.*, **111**, 4688.
4. Kathmann, S.M., Schenter, G.K., and Garrett, B.C., (2002) *J. Chem. Phys.*, **116**, 5046.
5. Kathmann, S.M., Schenter, G.K., and Garrett, B.C., (2005), *Phys. Rev. Lett.*, **94**, 116104.

This work was supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, of the U.S. Department of Energy. Battelle operates the PNNL for DOE.

MALTE – Model to Predict new Aerosol Formation in the Lower Troposphere

Michael Boy[1,2], Olaf. Hellmuth[3], Hannele Korhonen[4], Douglas Nilsson[5], Douglas ReVelle[6], Andrew Turnipseed[7], Frank Arnold[8] and Markku Kulmala [1]

[1]Department of Physical Sciences, Division of Atmospheric Sciences, P.O. Box 64, 00014 University of Helsinki, Finland
[2]ASP/ACD, NCAR, P.O. Box 3000, 80305 Boulder, Colorado, USA
[3]Leibniz Institute for Tropospheric Research, Permoserstrasse 15, 04 318 Leipzig, Germany
[4]Finnish Meteorological Institute, Air Quality Research, Sahaajankatu 20 E, FIN-00880 Helsinki, Finland
[5]Department of Meteorology, Stockholm University, S-106 91 Stockholm, Sweden
[6]Earth and Environmental Sciences, Los Alamos National Laboratory, P.O. Box 1663, MS D401, Los Alamos, NM, 87545 USA
[7]ACD, NCAR, 3450 Mitchell Lane, Boulder, CO 80301, USA
[8]Atmospheric Physics Division, Max-Planck Institute for Nuclear Physics, (MPIK), P.O. Box 103980, D-69029 Heidelberg, Germany

INTRODUCTION

New secondary particle formation has been observed at almost all places where both particle number concentrations and size distributions have been measured; a comprehensive summary of these studies is given in Kulmala et al. (2004). However, many questions currently remain to what extent these secondary aerosols can influence climate, radiative properties and human health. There is growing evidence that the Earth's radiation budget is affected by radiative forcing caused by changes in the number concentration and composition of aerosols. In addition higher number concentrations of ultra-fine particles could have a strong impact on the size distribution of cloud condensation nuclei which will further affect cloud properties.

Here we merged individually developed codes into a one dimensional model including aerosol dynamics, boundary layer meteorology and chemistry in order to investigate the formation and growth processes responsible for the secondary organic aerosols under realistic atmospheric conditions.

MODEL DESCRIPTION

MALTE is a one-dimensional model which includes several modules for the simulation of boundary layer dynamics and both chemical and aerosol dynamical processes.

For the description of Planetary Boundary Layer (PBL) processes, a first-order closure technique is applied. The PBL model includes predictive equations for four first statistical moments (means), i.e., the x- and y-component of the wind, the potential temperature and the specific humidity. The model is mainly based on the previous works of (Blackkader 1979) and ReVelle (1993). It considers geostrophic wind forcing, radiative forcing, and large-scale subsidence.

The aerosol dynamics are solved by the size-segregated aerosol model, UHMA (University of Helsinki Multicomponent Aerosol model - Korhonen et al., 2004). The model includes the major aerosol microphysical processes for a clear-sky atmosphere. It focuses on new particle formation and growth; thus, it incorporates both particle coagulation and multicomponent condensation. It applies a revised treatment of condensation flux onto free molecular regime particles, including activation of nano-sized clusters by organic vapours (Nano-Koehler theory). In the current version, kinetic nucleation of H_2SO_4 is the primary mechanism for the formation of new particles. It was determined that the predicted particle size distribution were in agreement with the measurements by using a value of $1x10^{-12}$ cm^3 s^{-1} for the kinetic coefficient. Particle dry deposition is also calculated. In order to account for deposition of newly formed particles, we have extrapolated former results to particle sizes less than 10 nm.

Currently there is a considerable lack of knowledge concerning the atmospheric oxidation of complex organic molecules such as monoterpenes or sesquiterpenes. The identities of the end-products, their reaction yields and their physical and chemical properties are not well-characterized. Therefore, in MALTE we have assumed a yield from monoterpene oxidation of 0.05 for all reaction products capable of condensing on nano-sized inorganic clusters (as determined using Nano-Koehler theory) and a yield of 0.05 for all products capable of being involved in the general condensation mechanism. These two yield values were found to give the best agreement for particle growth and size distribution with the measured values for the selected days.

RESULTS

Comparison of predicted and measured H_2SO_4 concentrations showed a satisfactory agreement. Further, the results indicate that the model is able to predict the on- and offset of new particle formation as well as the total aerosol number concentrations that were in good agreement with the observations (Figure 1).

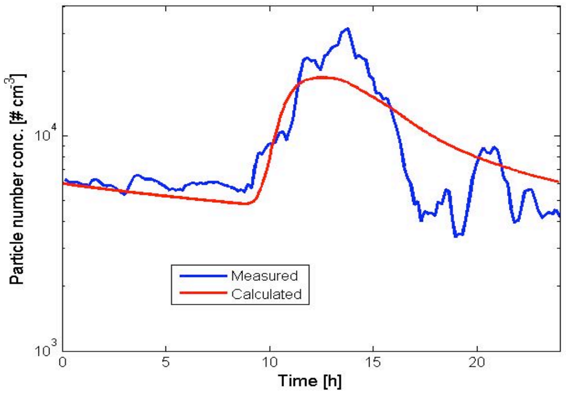

Figure 1. Measured and modelled total particle number concentration for the 26th of March 2003.

The simulations showed that at a certain transitional particle diameter (2-7 nm), organic molecules can begin to contribute significantly to the growth rate compared to sulphuric acid. At even larger particle sizes, organic molecules can dominate the growth rate on days with significant monoterpene concentrations. Similar results were published by Wehner and co-authors (Wehner et al., 2005) recently. They calculated that new particles needed to reach a size range between about 7 – 20 nm before it becomes apparent that organic vapours can contribute significantly to the growth rate. However, their observations were from a more urban site in Germany with up to twice as much H_2SO_4.

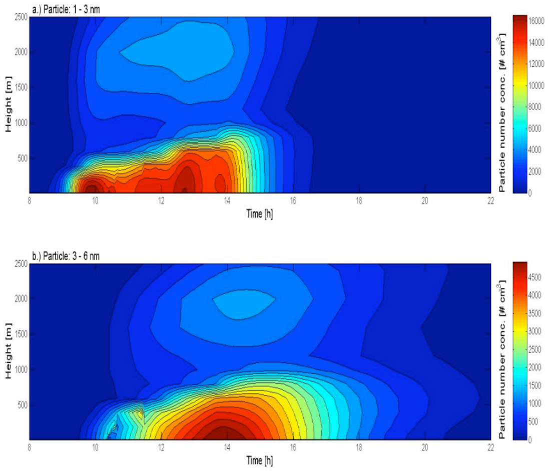

Figure 2. Vertical daily evolution of particle number concentrations in two different size ranges for the 26th of March 2003.

The intraday vertical evolution of new formed clusters and aerosols in two different size ranges resulted in two maxima at the ground (Figure 2). The results agree with measured vertical profiles between 11.21 and 11.31 for the same day reported by O'Dowd et al. (2005). The authors reported high number concentrations of particles between 3 to 6 nm from about 100 m (lowest flight height) up to 500 m and a decrease above.

CONCLUSIONS

This work presents a description of MALTE – a model to predict new aerosol formation in the lower troposphere. The results indicate that the model is able to predict new particle formation events in good agreement with observations.

The new version of the model also include the emission of organic vapours from the biosphere (MEGAN code from Alex Guenther), an improved organic chemical mechanism and a parameterization for ion-induced nucleation (PARNUC from Ned Lovejoy and Jan Kazil).

Keywords: *Boundary layer, Particle formation events*

REFERENCES

Blackadar, A.: Advances in Environmental Science and Engineering, Vol. 1, chap. High-resolution models of the planetary boundary layer, pp. 50–85, *Gordon and Breech Science Publishers, Inc.*, New York, 1979.

Korhonen, H., Lehtinen, K.E.J. and Kulamal, M.: Multicomponent aerosol dynamics model UHMA: modle development and validation, *ACP*, Vol. 4, pp 471-506, 2004.

Kulmala, M., Vehkamaeki, H., Petaejae, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: An observations, *J. Aerosol Sci.*, 35, 143–176, 2004.

O'Dowd, C. D., Yoon, Y. J., Junkermann, W., Aalto, P. P. and Lihavainen, H.: Airborne measurements of nucleation mode particles II: Boreal Forest Events, *Report Series in Aerosol Science*, Nr. 76, ISBN 952-5027-63-5, p. 162-173, 2005.

ReVelle, D.: Chaos and "bursting" in the planetary boundary layer, *J. Appl. Meteor.*, 32, 1169–1180, 1993.

Wehner, B., Petaja, T., Boy, M., Engler, C., Birmili, W., Tuch, T., Wiedensohler, A. and Kulmala, M.: The contribution of sulphuric acid and non-volatile compounds on the growth of freshly formed atmospheric aerosols, *Geo. Res. Let.*, Vol. 32, 2005.

Sensitivity of Modeled Number Concentrations to the Representation of New Particle Formation and Particle Emissions in Chemical Transport Models

Lim-Seok Chang, Douglas L. Wright, Ernie R. Lewis, Stephen E. Schwartz, and Robert McGraw
Atmospheric Science Division, Brookhaven National Laboratory,11973,USA

INTRODUCTION

Uncertainties in new particle formation (NPF) and emissions rates for particle number yield large uncertainties in modeled number concentrations (*N*). In this study, sensitivity studies were performed with a variety of approaches to NPF and several number emission rates using the Community Multiscale Air Quality (CMAQ) regional-scale model over all of the continental U.S with 60-km resolution for July 2004..

MODEL DESCRIPTION

NPF approaches included binary H_2SO_4–H_2O nucleation (Vehkamaki *et al.*, 2002; V02), ternary H_2SO_4–H_2O–NH_3 nucleation (Napari *et al.*, 2002; N02), and nucleation by ion-ion recombination (Turco *et al.*, 1998; NIIR). Newly-formed particles entered the Aitken mode at 3 nm diameter. The Kerminen and Kulmala (2002) parameterization for the ratio F_{KK02} of the NPF rate J_p at d_{npf} (3 nm in this work) to the nucleation rate J (1 nm) was included in some model variants. Empirical rates for the formation of 3–4 nm particles under clean conditions of the form $J_p = K[H_2SO_4]^n$, n=1, 2 (Eisele and McMurry, 1997; EM97) were also included. After calculating $J_p = F_{\mathrm{KK02}}\, J$ or $J_p = J$, the (constant) J_p over the 15-min time step was limited by the available H_2SO_4.

RESULTS

Overall model sensitivities were examined using average J_p and N over the domain and simulated period ($J_{p,\,\mathrm{ave}}$ and N_{ave}). The basecase J_p was the sum of the N02 and NIIR rates reduced by the factor F_{KK02}. Key results follow.

1. Using $J_p = F_{\mathrm{KK02}}\, J$ rather than $J_p = J$ reduced $J_{p,\,\mathrm{ave}}$ by a factor of ~3 and N_{ave} by a factor of ~2, even though the conversion is only to slightly larger (3-nm) size.
2. Replacing the ternary rate with the binary rate decreased $J_{p,\,\mathrm{ave}}$ by a factor ~0.05 but decreased N_{ave} by only ~0.4. Binary nucleation was usually negligible in the boundary layer (PBL); above the PBL the extent of binary nucleation approached that of ternary nucleation because of lower temperatures and $[NH_3]$.
3. When the binary nucleation rate was used, inclusion of NIIR increased both $J_{p,\,\mathrm{ave}}$ and N_{ave} only modestly.
4. The NPF rate of the average of the two n = 2 curves of Fig. 7 of EM97 yielded $J_{p,\,\mathrm{ave}}$ intermediate between that of the binary and ternary parameterizations in the PBL, and comparable to the binary $J_{p,\,\mathrm{ave}}$ above the PBL.
5. Reducing the mean diameter of emitted particles by a factor of two (for fixed mass emission rate) for both the Aitken and accumulation modes gave a modest decrease in both $J_{p,\,\mathrm{ave}}$ and N_{ave}. This resulted from increased surface area and reduced NPF when emitted mass is apportioned into smaller particles. Increasing the emitted mean diameter increased $J_{p,\,\mathrm{ave}}$ and N_{ave}.
6. Particle transfer from the Aitken to the accumulation mode is necessary in modal models to maintain distinct modes. Transfer is not governed by a physical process, and for large NPF rates this introduces a substantial uncertainty in accumulation mode number.
7. When the NPF rate is large, the subsequent reduction of J_p due to limited H_2SO_4 was also large with the 15-min time step. Nucleation and condensation are partially operator-split in CMAQ. When its binary nucleation rate is replaced by the N02 ternary rate, H_2SO_4 consumption is biased in favor of NPF.
8. In the Aitken mode, average NPF and coagulation rates nearly balanced. In the accumulation mode, number emissions and intermodal transfer were balanced by wet deposition.

CONCLUSIONS

New particle formation dominates uncertainties in Aitken mode number concentration, whereas conversion of mass emission rates to number emission rates dominates uncertainties in accumulation mode number.

Keywords: *New particle formation*

REFERENCES

Eisele, F. L., McMurry, P. H. (1997). Recent progress in understanding particle nucleation and growth, *Phil, Trans. R. Soc. Lond*. B 252, 191-201.

Napari, I., Noppel, M., Vehkamaki, H., Kulmala, M. (2002). Parameterization of ternary nucleation rates for H_2SO_4-NH_3-H_2O vapors, *J. Geophys. Res.*, 107, D19, 4831, doi:10.1029/2002JD002132.

Turco, R. P., Zhao, J. X., Yu, F. (1998). A new source of tropospheric aerosols: Ion-ion recombination, *Geophys. Res. Letters*, 25, 635-638.

Vehkamaki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J. , Timmreck, C. Noppel, M., and Laaksonen, A. (2002). An improved parameterization for sulfuric acidwater nucleation rates for tropospheric and stratospheric conditions, *J. Geophys. Res.*, 107, D22, 4622, doi:10.1029/2002JD002184.

Evaluation of Homogeneous Nucleation Parameterizations used in 3-D Air Quality Models

Yang Zhang
Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695, USA

INTRODUCTION

Three-dimensional (3-D) modeling of particulate matter (PM) properties (e.g., mass, number, and size distribution) is a formidable task because of the complexity of its physical and chemical processes and the demand for large computational resources. While most 3-D air quality models (AQMs) can reproduce the mass concentrations of PM with an aerodynamic diameter within 2.5 μm and 10 μm (i.e., $PM_{2.5}$ and PM_{10}) within 50% of the measurements, accurately simulating particle number concentrations and size distributions remains challenging. One of the large uncertainties lies in the model treatment of new particle formation process due to homogeneous nucleation. Use of different nucleation parameterizations in 3-D models introduces significant uncertainties in the predicted number production rates and number concentrations of $PM_{2.5}$, particularly in the nuclei mode (Zhang et al., 1999). Those parameterizations are derived either empirically from laboratory experiments or from kinetic models that are based on classical binary and ternary nucleation theories.

In this work, six binary and one ternary homogeneous nucleation parameterizations are examined first in a box model and then in the 3-D Models-3/Community Multiscale Air Quality (CMAQ) modeling system. The six binary homogeneous nucleation parameterizations are those of Wexler et al. (1994), Pandis et al. (1994), Fitzgerald et al. (1998), Harrington and Kreidenweis (1998), Kulmala et al. (1998), and Vehkamäki et al. (2002), and the ternary nucleation parameterization is Napari et al. (2002). All the six binary parameterizations have been used in 3-D AQMs such as CMAQ, the California/Carnegie-Mellon Institute of Technology Air Quality Model (CIT), and the Gas, Aerosol, Transport, radiation, General Circulation, Mesoscale, and Ocean Model (GATOR-GCMOM). The parameterizations of Pandis et al. (1994), Fitzgerald et al. (1998), Vehkamäki et al. (2002), and Napari et al. (2002) are implemented into CMAQ and compared with two existing parameterizations in CMAQ (i.e., Kulmala et al. (1998) in CMAQ v4.4 and Harrington and Kreidenweis (1998) in all versions prior to v4.4). The 12-28 June 1999 Southern Oxidants Study (SOS) episode is selected as a testbed to evaluate the PM number and size predictions of CMAQ with the six parameterizations. The predicted number concentrations and size distributions of PM are evaluated against measurements from the Aerosol Research and Inhalation Epidemiology Study (ARIES) (McMurry et al., 2000; Woo et al., 2001). The statistical measures are calculated and analyzed for the total number, volume, and surface areas of $PM_{2.5}$ as a sum of the Aitken- and accumulation-mode PM and those of PM in individual segregated size sections over the diameter range of 0.00306 to 2 μm that was used in the ARIES measurements for PM_2.

EVALUATION RESULTS

Significant differences are found among the binary nucleation rates calculated with different parameterizations and between the binary and ternary nucleation rates (e.g., by up to 3-7 orders of magnitude under specific conditions). For example, at RH = 50% and T = 298.15 K, all binary parameterizations except Wexler et al. (1994) show a strong dependence on N_{H2SO4}. While Fitzgerald et al. (1998) shows large deviations from the ternary nucleation rates for NH_3 = 100 ppt, Pandis al. (1994) gives a very close agreement to the ternary nucleation rates for NH_3 = 1 ppt. For nucleation rates $> 1 \times 10^{-8}$ cm^3 s^{-1}, the nucleation rates predicted by Kulmala et al. (1998) are lower by 1-2 orders of magnitude compared with those of Vehkamäki et al. (2002) and by 3-6 orders of magnitude compared with those of Fitzgerald et al. (1998).

Table 1 summarizes the 3-D model simulation results. All nucleation parameterizations significantly underpredict (by a factor of 1.4 to 47) the total number concentrations of Aitken-mode PM and overpredict (by a factor of 1.38 to 1.74) those of accumulation-mode PM. The PM number predictions with different nucleation parameterizations can differ by 4 and 1.5 orders of magnitude for Aitken- and accumulation-mode PM, respectively, with the lowest by Kulmala et al. (1998) and the highest by either Harrington and Kreidenweis (1998) or Napari et al. (2002). The ternary nucleation parameterization gives the best overall performance in predicting PM number and size distributions in terms of both temporal variations and performance statistics.

Major atmospheric processes and their relative impact on predicted PM number and size distribution are analyzed through the Integrated Process Rate (IPR) analysis and sensitivity studies. IPR analysis shows that controlling processes are different for Aitken-mode vs. accumulation-mode, number vs. volume vs. surface areas, and urban/upwind locations vs. rural/remote /downwind locations. For example, in southeastern U.S., at urban/upwind locations, the production of Aitken-mode number is dominated by PM processes and vertical transport, and its loss is dominated by dry deposition. At rural/remote and/or downwind locations, vertical transport, horizontal transport, and aqueous-phase processes are major production processes for Aitken-mode PM number; and its loss is controlled by dry deposition and PM processes.

Table 1. Performance statistics for hourly $PM_{2.5}$ number concentrations predicted by CMAQ with various nucleation parameterizations at the surface during June 14-28, 1999[1].

a. Aitken Mode

	Nuclk0	Nuclh1	Nuclv2	Nuclp3	Nuclf4	Nucln5
Obs	36507	36507	36507	36507	36507	36507
Mod	770	22002	986	2949	2150	26237
Data #	306	306	306	306	306	306
NMB	-0.98	-0.397	-0.97	-0.92	-0.94	-0.28
NME	0.98	1.044	0.97	0.92	0.94	1.30
NMBF	-46.44	-0.659	-36.01	-11.38	-15.98	-0.39
NMEF	46.44	1.732	36.01	11.38	15.98	1.80

b. Accumulation Mode

	Nuclk0	Nuclh1	Nuclv2	Nuclp3	Nuclf4	Nucln5
Obs	1805	1805	1805	1805	1805	1805
Mod	2481	2963	2494	2783	2736	3144
Data #	329	329	329	329	329	329
NMB	0.38	0.64	0.38	0.54	0.52	0.74
NME	0.73	0.82	0.73	0.77	0.76	0.91
NMBF	0.38	0.64	0.38	0.54	0.52	0.74
NMEF	0.73	0.82	0.73	0.77	0.76	0.91

[1] Nuclk0- Kulmala et al. (1998); Nuclh1- Harrington and Kreidenweis (1998), Nuclv2- Vehkamäki et al. (2002), Nuclp3- Pandis et al. (1994), Nuclf4-Fitzgerald et al. (1998), and Nucln5-Napari *et al.* (2002). NMB/NME-Normalized mean bias/error; NMBF/NMEF-Normalized mean bias factor/error factor.

Sensitivity simulations provide the relative importance of the assumed initial PM size distribution and several atmospheric processes including emissions, cloud scavenging, dry deposition, and coagulation in simulating PM number concentrations and size distributions. Among these processes and parameters, the PM number and size distribution predictions are most sensitive to coagulation, emission, and the assumed initial PM size distribution, and relatively insensitive to cloud scavenging and dry deposition. For example, coagulation can destroy total numbers of Aitken- and accumulation-mode, 88.24% and 66.35%, respectively at an urban location such as Jefferson Street in Atlanta and 97.32% and 74.58%, respectively at a remote location such as Great Smoky Mountain. Neglecting coagulation significantly overpredicts PM number and surface concentrations for Aitken- and accumulation-mode PM, overpredicts Aitken-mode volume concentrations and underpredicts accumulation-mode volume concentrations because of lack of growth from Aitken-mode to accumulation-mode.

CONCLUSIONS

Various homogeneous nucleation parameterizations predict nucleation rates that differ by several orders of magnitude, posting challenges in accurately simulating PM number concentrations and size distributions. Cautions are advised in selecting those parameterizations for 3-D AQM applications since most parameterizations have not been rigorously tested for all ranges of ambient conditions mainly because of lack of data. Observations are urgently needed for a systematic evaluation of their performance.

ACKNOWLEDGEMENTS

This research was performed under the NSF Award No. Atm-0348819, and the Memorandum of Understanding between the U.S. EPA and the U.S. Department of Commerce's NOAA and under agreement number DW13921548. Thanks are due to Alan Hansen, EPRI, for permitting the use of the ARIES data. Thanks are due to Mark Z. Jacobson, Peter McMurry, Prakash V. Bhave, Shaocai Yu, and Ken L. Schere, for insightful discussions and comments on this work.

Keywords: *Homogeneous Nucleation Parameterizations, 3-D Air Quality Modeling, Evaluation, Process Analysis*

REFERENCES

Fitzgerald, J.W., W.A. Hoppel, and F. Gelbard (1998), A one-dimensional sectional model to simulate multicomponent aerosol dynamics in the marine boundary layer. 1. Modal description, *J. Geophys. Res.*, *103*, 16085-16102.

Harrington, D.Y., and S.M. Kreidenweis (1998), Simulation of Sulfate Aerosol Dynamics. I. Model Description. *Atmos. Environ.*, *32*, 1691-1700.

Kulmala M., A. Laaksonen, and L. Pirjola (1998), Parameterizations for sulphric acid/water nucleation rates, *J. Geophys. Res.,* 103, 8301-8308.

McMurry, P.H., K.S. Woo, R. Weber, D.-R. Chen, and D.Y.H. Pui (2000), Size distributions of 3-10 nm atmospheric particles: implications for nucleation mechanisms, *Phil. Trans. R. Soc.*, London, A358: 2625-2642.

Napari, I., M, Noppel, H. Vehkamäki, and M. Kulmala (2002), Parameterization of ternary nucleation rates for H_2SO_4-NH_3-H_2O vapors. *J. Geophys. Res., 107,* 4381.

Pandis, S.N., L.M. Russell, and J.H. Seinfeld (1994), The relationship between DMS flux and CCN concentration in remote marine regions, *J. Geophys. Res.*, 99, 16945-16957.

Vehkamäki, H., M. Kulmala, I. Napari, K.E.J. Lehtinen, C. Timmreck, M. Noppel and A. Laaksonen (2002), An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, *J. Geophys. Res.*, *107*, 4622, doi:10.1029/2002JD002184.

Wexler, A.S., F.W. Lurmann, and J.H. Seinfeld (1994), Modeling Urban and Regional Aerosols. I. Model Development. *Atmos. Environ. 28*, 531-546.

Woo, K.S., D.R., Chen, D.Y.H., Pui, P.H. McMurry (2001), Measurement of Atlanta aerosol size distributions: observations of ultrafine particle events. *Aerosol Sci. Technol.*, 34, 75-87.

Zhang, Y., C. Seigneur, J.H. Seinfeld, M.Z. Jacobson, and F.S. Binkowski (1999), Simulation of aerosol dynamics: A comparative review of algorithms used in air quality models, *Aerosol Sci. Technol.*, 31, 487-514.

Title: A new nano-SMPS system for measuring size distribution of atmospheric aerosols below 3nm

Kenjiro Iida, Mark R. Stolzenburg, and Peter H. McMurry
Department of Mechanical Engineering, University of Minnesota, 55455, Minneapolis, USA

ABSTRACT

We are developing a new Nano-SMPS system that detects sub 3 nm particles and samples at high particle count rate. Efforts also have been made to make the system safe, stable, and user friendly. The system consists of an aerosol charger, differential mobility analyzer (DMA), and condensation particle counter (CPC) (Figure 1). The aerosol charger is based on the surface discharge microplasma aerosol charger (SMAC) operating in the negative unipolar charging mode. The major advantage of the SMAC is that it does not use a radioactive source. The original design of *Kwon et al,* (2006) was modified to simultaneously trap the large primary particles and enhance interactions between the sampled particles and generated ions. The design of the mobility classifier region is based on the radial DMA (*Zhang et al.,* 1995). The effect of wall diffusion losses within the channel between the changer and classifier is minimized by extracting the core portion of the annular flow at the aerosol inlet slit. The classifier region is designed to maximize the sheath flowrate without causing secondary flow formation. The geometry of the aerosol inlet slit at the confluence of the sheath flow and the aerosol inlet flow was redesigned to ensure that two flows merge smoothly. The height of the classifying disks will be adjusted to choose the height that gives the best mobility resolution. We tentatively plan to use a laminar flow CPC (LCPC) because LCPCs have performed stably during our past sampling campaigns. However, the modular design of the new SMPS system will also accommodate turbulent Mixing CPC that has recently been shown to detect particles as small as 1nm at high count rates (*Kim et al.,* 2003; *Sgro and Fernandez de la Mora* 2004). We will choose a CPC working fluid that gives the lowest minimum detectable size. The overall detection efficiency of the entire system, non-ideality in voltage mobility relation and mobility resolution will be experimentally determined by tandem differential mobility analysis (TDMA) experiments.

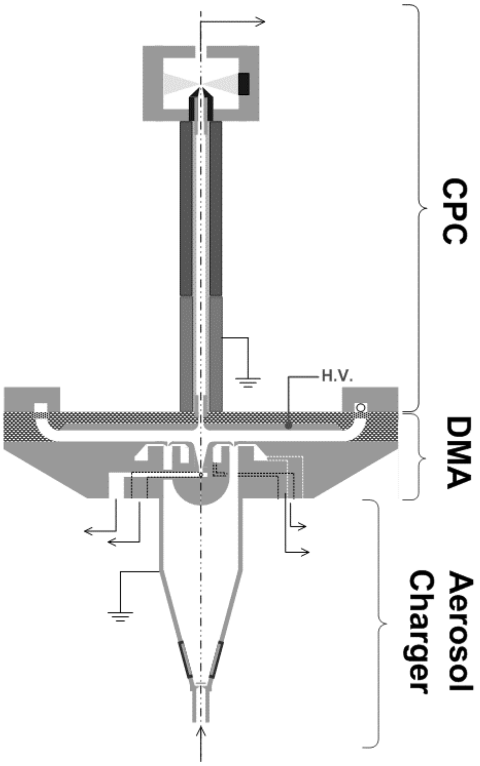

Figure 1: Schematics of the nano-SMPS system

REFERENCE:

Kim, C. S., K. Okuyama and J. Fernandez de la Mora (2003), Performance evaluation of an improved particle size magnifier (PSM) for single nanoparticle detection, *Aerosol Sci. Technol., 37*, 791-803.

Kwon, S. B., H. Sakurai and T. Seto (2006a), Unipolar charging of nanoparticles by the Surface-discharge Microplasma Aerosol Charger (SMAC), *submitted to J. Aerosol Sci.,*

Sgro, L. A. and J. Fernandez de la Mora (2004), A Simple Turbulent Mixing CNC for Charged Particle Detection Down to 1.2 nm, *Aerosol Science and Technology, 38(1)*, 1, 1-11.

Zhang, S.-H., Y. Akutsu, L. M. Russell, R. C. Flagan and J. H. Seinfeld (1995), Radial differential mobility analyzer, *Aerosol Sci. Technol., 23*, 3, 357-72.

Measuring Aerosol Particles below 3 nm by Condensation Particle Counter UF–02proto

Mikko Sipilä, Tuukka Petäjä, Hanna Manninen, Genrik Mordas, Ilona Riipinen and Markku Kulmala
Department of Physical Sciences, University of Helsinki, PO Box 64, 00014 Helsinki, Finland

INTRODUCTION

Condensation particle counters (CPC) are widely used in atmospheric aerosol particle measurements. Typically particle size range starting from 3 nm can be covered with commercial instruments. Charged particles or clusters smaller than 3 nm can be measured by ion spectrometers but detection of neutral clusters smaller than 3 nm has turned out to be quite complicated. In this paper we describe the studies of detection efficiency of UF–02proto conductive cooling type CPC. The instrument is described in detail by Mordas *et al*. (2005). Results from the field measurements with UF–02proto are presented by Riipinen *et al.* (2006).

EXPERIMENT

A tube furnace was used to generate polydisperse silver aerosol. At approximately 980ºC silver evaporated into 5 l min^{-1} nitrogen flow. After the heating section of the furnace the flow cooled down and silver vapour started to nucleate. To prevent the growth of the particles to bigger sizes the flow was diluted immediately after the furnace by ca. 15 l min^{-1} of purified compressed air. As a result a particle distribution with the mode around 2.5 nm (mobility equivalent diameter) was achieved.

After passing through the neutralizer (^{241}Am) a monodisperse fraction was extracted from the aerosol in a differential mobility analyzer (DMA). An aerosol electrometer was used as a reference.

Because the transfer functions of the DMA are reasonably wide at the particle sizes close to 2 nm (Stolzenburg, 1988, Reischl *et al.*, 1997) a simple correction that takes account of the initial distribution was applied.

Detection efficiency was investigated at constant condenser temperature (T_{cond} = +10ºC) and at saturator temperatures from +43 ºC up to +62 ºC.

RESULTS

Typical detection efficiency curve is presented in Fig. 1. At normal operation conditions (T_{cond} = +10ºC, T_{sat} = +43ºC) a 50%–detection limit of (4.2±0.4) nm was reached. Increasing the saturator temperature finally led to (1.8±0.2) nm detection limit at saturator temperature of +54ºC. After that the heating of the saturator did not any more affect the detection limit, but homogeneous nucleation rate started to increase slowly. Measurement with T_{sat} = 62ºC was conducted with background aerosol (ca. 15 nm particles) concentration of 4000 cm^{-3} to prevent homogeneous nucleation.

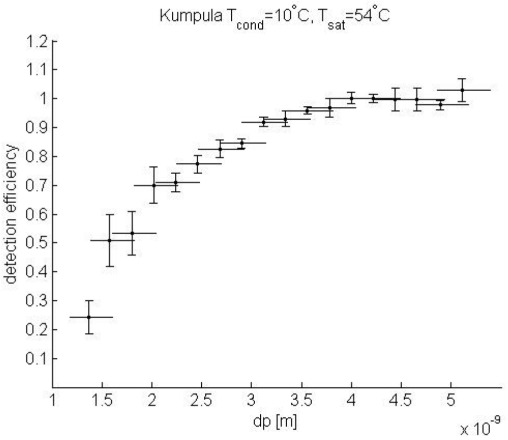

Figure 1. Detection efficiency as a function of particle size with 44 ºC temperature difference between saturator and condenser.

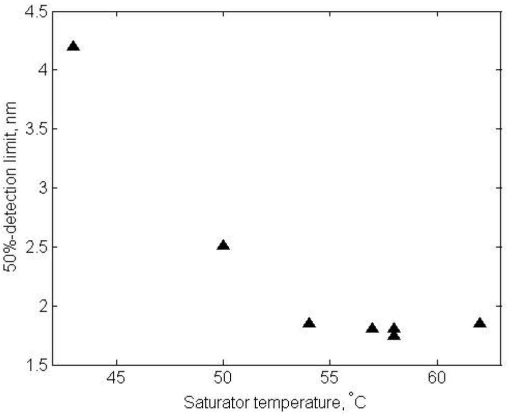

Figure 2. 50%–detection limit as a function of saturator temperature when condenser temperature is kept constant (+10ºC). In case of saturator temperature of 62 ºC a background aerosol (4000 cm^{-3}, diameter ca. 15 nm) was used to prevent homogeneous nucleation.

DISCUSSION

It is obvious that aerosol was not completely saturated with butanol vapour in saturator, thus high temperature differences were needed before homogeneous nucleation started to dominate over the heterogeneous nucleation on calibration aerosol particles.

It should be mentioned that these calibrations were performed using negatively charged particles. It is known fact that activation of charged particles can take place with lower supersaturations than activation of neutral ones. Thus the 50%–detection limit of (1.8±0.2) nm obtained in this study is very probably slightly different for neutral particles.

Also, one should keep in mind that the particle diameter in size range below 3 nm is not a well defined concept. In this study particle diameter is expressed as mobility equivalent diameter (Millikan – Fuchs diameter) whereas application of e.g. Tammet's mobility-diameter conversion (Tammet, 1995) would lead to very different diameters. As an example 1.8 nm mobility equivalent diameter corresponds to Tammet's diameter of ca. 1.5 nm.

CONCLUSIONS

Despite of all small obscurities related to particle sizes, performed detection efficiency studies show that with UF–02proto CPC 50%–detection limits far below 3 nm can be reached.

Keywords: *Condensation particle counters, Detection efficiency, Neutral clusters*

REFERENCES

Mordas, G, Kulmala, M. Petäjä, T. *et al.* (2005). Design and performance characteristics of a condensation particle counter UF-02proto, *Boreal Environment Research*, 10, 543-552.

Reischl, G. P., Mäkelä J. M. and Necid, J. (2002) Performance of Vienna type differential mobility analyzer at 1.2-20 nanometer, *Aerosol Sci. Technol.*, 27, 651-672.

Riipinen, I., Kulmala, M. Manninen, H. *et al.* (2006). Towards observations of neutral atmospheric clusters: Results from Hyytiälä, Southern Finland, *These proceedings.*

Stolzenburg, M. R. (1988) *An ultrafine aerosol size distribution measuring system*, Ph. D. Thesis, Univ. of Minnesota.

Tammet, H. (1995) Size and mobility of nanometer particles, clusters and ions, *J. Aerosol Science*, 26, 459-475.

Direct Measurement of Neutral Molecular Clusters by Chemical Ionization Mass Spectrometry: Elucidating the Mechanisms of New Particle Formation in the Atmosphere.

Mari E. Titcombe[1], Jeffrey T. Roberts[1], Peter H. McMurry[2], Lee Mauldin[3] and Fred R. Eisele[3]
[1]Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, USA
[2]Department of Mechanical Engineering, University of Minnesota, 111 Church Street, S. E., Minneapolis, MN 55455, USA
[3]Atmospheric Chemistry Division, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307, USA

According to the Intergovernmental Panel on Climate Change, direct and indirect aerosol radiative forcing effects have the greatest associated uncertainties in climate change predictions (Houghton *et al*., 2001). Recent work has shown that new particle formation can significantly enhance concentrations of cloud condensation nuclei, thereby contributing to the aerosol "indirect" effect. Modeling of cloud condensation nuclei (CCN) from a variety of sources and atmospheric environments is hindered by inadequate fundamental understanding of processes that lead to new particle formation and growth (Prenni *et al*., 2001; Andronache *et al*., 1997; Rotstayn *et al*., 2002; Stott *et al*., 2000; and Kulmala *et al*., 2004). Current size detection limits in standard particle sizing instrumentation, such as condensation nuclei counters (CNC) (Stolzenburg and McMurry, 1991) and differential mobility analyzers (DMA) (Chen *et al*., 1996), prohibit the direct measurement of neutral clusters smaller than 3nm. Freshly nucleated particles have diameters of roughly 1nm, resulting in a lag between actual particle nucleation and particle growth to detectable sizes. This 2nm growth may occur on the order of minutes up to an hour (Kulmala, *et. al*., 2004) leading to an uncertainty in the chemical and physical conditions at the time of nucleation. The intent of this research is to further elucidate the chemical and physical characteristics of nucleation in the atmosphere. Recently developed instrumentation allows the direct measurement of neutral molecular clusters (Eisele *et. al*., 2000; Hanson *et. al*., 2002). Based on this earlier work, we are building a new chemical ionization mass spectrometer (CIMS) to carry out laboratory measurements of clusters formed by nucleation. The use of a transverse drift system inlet will allow for the differentiation of neutral clusters formed in the reactor from those formed by ion-induced processes in the source. Cluster size distributions for the binary H_2SO_4-H_2O, and ternary H_2SO_4-H_2O-NH_3 systems will be measured. A pseudo-batch reactor will provide cluster formation at near ambient gas concentrations. Cluster growth will proceed on the time scale of atmospheric events. Cluster size distributions will be measured in varying physical conditions to examine the temperature, humidity and concentration dependence of cluster growth. The effects of ammonia and/or organic amines on cluster formation and growth will be examined. As one component of collaborative research, the laboratory CIMS results will be complimented with atmospheric measurements. By combining these measurements of clusters with measurements of nanoparticles with the new scanning mobility particle sizer (nano-SMPS) being developed by Iida and McMurry (2006), we aim to "bridge the gap" between the measurements of molecules and nanoparticles. A goal of this collaborative research is the comparison of size distribution data to concurrently developed models of nucleation and growth rate coefficients.

Keywords: nucleation, sulfuric acid, ammonia, particle formation, chemical ionization mass spectrometry, neutral molecular clusters

REFERENCES

Andronache, C.; Chameides, W. L. (1997) *J. Geophys. Res., 102(D17)*, 21443.

Chen, D.R.; Pui, D. Y. H.; Hummes, D.; Fissan, H.; Quant, F. R.; Sem, G. J. (1996) *Nanometer Differential Mobility Analyzer: Design and Numerical Modeling.* AAAR, Orlando, Florida.

Dockery, D. W.; Pope, C. A. III. (2006) *J. Air & Waste Management Assoc.*, *56*, 709.

Dominici, F.; Peng, R. D.; Bell, M. L.; Pham, L.; McDermott, A.; Zeger, S. L.; Samet, J.M. (2006) *J. American Medical Association.*, *295(10)*, 1127.

Eisele, F. L.; Hanson, D. R. (2000) *J. Phys. Chem.*, *104*, 830.

Hanson, D. R.; Eisele, F. L (2002) *J. Geophys. Res.*, *107(D12)*, 4158.

Houghton, J. T.; Ding, Y.; Griggs, D.J.; Noguer, M.; van der Linden, P.J.; Dai, X.; Maskell, K.; Johnson, C.A. (2001) *Climate Change 2001, The Scientific Basis*; Intergovernmental Panel on Climate Change, Cambridge, University Press: Cambridge.

Kulmala, M.; Vehkamaki, H.; Petaja, T.; Dal Maso, M.; Lauri, A.; Kerminen, V. M.; Birmili, W.; McMurry, P. H. (2004) *J. Aerosol Sci.*, *35*, 143.

Prenni, A. J.; DeMott, P. J.; Kreidenweis, S. M.; Sherman, D. E.; Russell, L. M.; Ming, Y. (2001) *Journal of Physical Chemistry A.*, *105(50)*, 11240.

Rotstayn, L. (2002) *J. Geophys. Res.*, *107(D21)*, 4592.

Steib, D. M.; Judek, S.; Burnett, R. T. (2002) *J. Air & Waste Management Assoc.*, *52(4)*, 470.

Stolzenburg, M.R.; McMurry, P.H. (1991) *Aerosol Sci. Technol., 14*, 48.

Stott, P. A.; Tett, S. F.; Jones, G. S.; Allen, M. R.; Mitchell, J. F.; Jenkins, G. J. (2000) *Science*, *290(5499)*, 2133.

This work is supported by the National Science Foundation.

Aerosol Mass Spectrometry of New Particle Growth

Douglas R. Worsnop
Aerodyne Research, Inc., Billerica MA 01821

INTRODUCTION

One of the major goals in research in new particle formation and growth in the atmosphere is the identification of the chemical composition of newly formed aerosol, from critical clusters to ultrafine particles. In fact, chemical measurement of the gas phase precursors is equally important. In both phases, it is a truism that the importance of the measurements is matched by practical experimental difficulties. Here we present two case studies of mass spectrometric determination of new particle chemical composition showing contrasting organic and inorganic particle growth events. Though instrumentally limited to observation of relatively large particles (>30 nm diameter), these results highlight the range of atmospheric aerosol chemistry during new particle formation events.

These field studies deployed an aerosol mass spectrometer (AMS, Jayne et al, 2000) that utilizes an aerodynamic lens that can focus particles in the size range 40 to 1000nm (Liu et al,1995, Zhang et al, 2004). This approach differs from other mass spectrometer instruments which detect the composition smaller particles (<10 nm), both neutral and charged (that will be discussed in detail elsewhere at this workshop). The advantage of the AMS is the capability of measuring the complete non-refractory chemical composition of sub-micron aerosol, providing chemical balance in combining SMPS volume and AMS mass aerosol loading. (see for example, Jimenez et al, 2003).

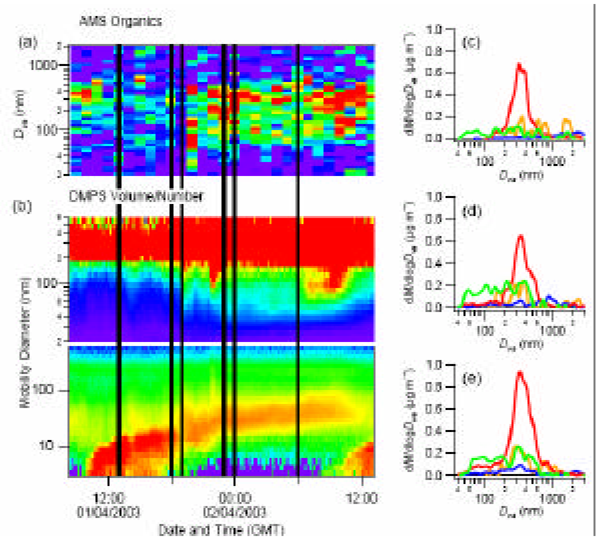

Figure. 1. Hyytialla growth event (1 April, 2003) observed by the AMS (a) and DMPS (b). Colour scheme as in Fig. 2. Distributions (c), (d) and (e) are from 13:00–18:00, 19:00–23:00 and 00:00–06:00GMT respectively. Note Composition in the Aitken mode is partly inorganic during the later stages.

RESULTS

Figures 1 and 2 display results from particle nucleation and growth events observed at forest and urban sites; Hyytiala, Finland (QUEST, 2003) and Pittsburgh in the U.S (PAQS, 2002), respectively. Panels (a) and (b) in Figure 1 (Allan et al, 2006) compare the time evolution of AMS mass and SMPS size distributions for a late morning formation event with aerosol growth continuing through the night. Average mass distributions (panels (c)-(e)) show that the AMS is sensitive only after particle growth to >40 nm (vacuum aerodynamic diameter), corresponding to SMPS number mode >20nm diameter. In this forested environment, the appearance of ultrafine particles (<200nm) after noon is clearly dominated by organics, with subsequent growth after midnight largely to sulfate (and some nitrate). (Note that the appearance of ultrafine organic mass mode is distinct from the background accumulation mode that is predominantly sulfate). Moreover, the mass spectrum of the organics appears consistent with biogenic sources as indicated by filter analyses (Allan et al., 2006 and references therein).

Figure 2 shows the time evolution of the fractional chemical composition of growing particles (33-60nm vacuum aerodynamic diameter) following a nucleation event in Pittsburgh (Zhang et al, 2004). In this case, the overall aerosol microphysics was more complex, with multiple size modes, resolved in size and compositions arising from traffic emission, new particle growth and aged accumulation. However, the distinct change in ultrafine particle composition after 9am was clearly associated with the growth of a nucleation event (at 8am) as indicated by a signature in

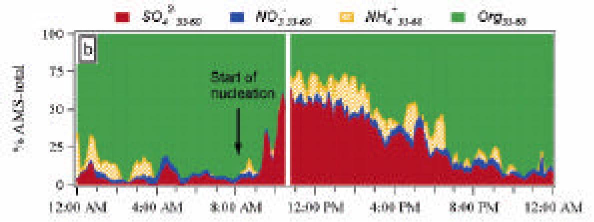

Figure. 2 Fractional chemical composition for Pittsburgh nucleation/growth event September 12, 2002. Percent fraction of chemical species vs total (sulfate + nitrate + ammonium + organics) in 33-60 nm (D_{va}) particles. Note ammonium appears only after 11am.

the SMPS distribution similar to the one shown in Figure 1b (see Zhang et al, 2004). In this urban case, the initial particle growth > 40nm (between 9 and 11 am) is dominated by sulfuric acid, reflecting the regional sources of SO_2 surrounding the city of Pittsburgh.

There are two points to be made about the results in Figures 1 and 2. First, the composition of the growth mode (>40nm) cannot be directly related to that in the initial nucleation event; AMS detection is not sensitive to nucleation particles On the other hand, observed growth mode chemistry does appear to reflect the condensable vapors expected at each site under the "clean" conditions necessary for nucleation – organics (likely biogenic) in a forest and sulfate in the Eastern U.S. Moreover, in both cases it is apparent that the condensable vapor chemistry evolves as emissions and processing change the air mass. For example, while Figure 2 indicated there was insufficient NH_3 vapor to neutralize condensed aerosol H_2SO_4 in the morning on September 12, 2002, results from an event 4 days earlier showed the initial aerosol growth was in fact neutralized $(NH_4)_2SO_4$ (Zhang et al, 2004). In the Hyytiala case, subsequent growth overnight shifted to inorganics, in contrast to organics earlier in the day.

CONCLUSIONS

The challenge is to extend these results to smaller particles, corresponding to earlier stages of new particle formation and growth. Recent developments in aerodynamic lens design hold promise in extending transmission for mass spectrometric analysis of nanoparticles (Wang et al, 2005a; 2005b). At the same time, absolute detection sensitivity limits must also be improved in order to detect smaller particles (see for example, Drewnick et al, 2005).

Beyond the technical challenges of coupling the sampling and chemical detection of nanometer sized particles, it is important to note that the experimental separation of the gas and particle phases can be problematic in the limit of low concentration and small particles involved in nucleation/growth events. At near ppt mixing ratios – representative both of gas phase precursors and nanometer particles - partitioning between the gas and aerosol phases is extremely sensitive to perturbations in temperature and relative humidity during aerosol sampling and detection.

Keywords: *Ultrafine Aerosol, Aerosol Growth, Mass Spectrometry*

REFERENCES

Allan, J.D., M. R. Alfarra, K. N. Bower, H. Coe, J. T. Jayne, D. R. Worsnop, P. P. Aalto, M. Kulmala, T. Hyötyläinen, F. Cavalli, A. Laaksonen (2006) Size and composition measurements of back-ground aerosol and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer,. *Atmos. Chem. and Phys*, 6, 315-327.

Drewnick, F., Hings, S. S., DeCarlo, P., Jayne, J. T., Gonin,M., Fuhrer, K., Weimer, S., Jimenez, J. L., Demerjian, K.L.,Borrmann, S., and Worsnop, D. R.: A New Time-of-Flight (2005) Aerosol Mass Spectrometer (TOF-AMS)-Instrument Description and First Field Deployment, *Aerosol Sci. Technol.*, 39, 637–658.

Jayne, J. T., Leard, D. C., Zhang, X. F., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R. (2000) Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Technol.*, 33, 49–70.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W., and Davidovits, P.: (2003) Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, *J. Geophys. Res.-Atmos.*, 108, 8425, doi:10.1029/2001JD001213, 2003.

Liu, P., Ziemann, P. J., Kittelson, D. B., and McMurry, P. H.: (1995) Generating Particle Beams of Controlled Dimensions and Divergence:II. Experimental Evaluation of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, *Aerosol Sci. Technol.*, 22, 314–324,.

Wang, X., F.E. Kruis, and P.H. McMurry (2005a) Aerodynamic Focusing of Nanoparticles: I. Guidelines for Designing Aerodynamic Lenses for Nanoparticles *Aerosol Sci. and Techno.y*, 39:611–623.

Wang, X., Gidwani, A. Girshick, S.L., and McMurry P.H. (2005b) Aerodynamic Focusing of Nanoparticles: II. Numerical Simulation of Particle Motion Through Aerodynamic Lenses *Aerosol Sci. and Techno.y*, 39:624–36.

Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., and Jimenez, J. L. (2004) Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry, *Environ. Sci. Technol.*, 38, 4797–4809.

Zhang, X. F., Smith, K. A., Worsnop, D. R., Jimenez, J. L., Jayne, J. T., Kolb, C. E., Morris, J., and Davidovits, P.: Numerical characterization of particle beam collimation: Part II – Integrated aerodynamic-lens-nozzle system, (2004) *Aerosol Sci. Technol.*, 38, 619–638.