Towards a molecular understanding of atmospheric aerosols

677. WE-Heraeus-Seminar

Aug. 26 to Aug. 31, 2018
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm and Else Heraeus Foundation (Wilhelm und Else Heraeus-Stiftung) is a private foundation which supports research and education in science, especially in physics. A major activity is the organization of seminars. To German physicists the foundation is recognized as the most important private funding institution in their fields. Some activities of the foundation are carried out in cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft).

Scope of the 677. WE-Heraeus-Seminar:

Environmental quality and climate change are major global challenges that society faces today. Currently, severe knowledge gaps in fundamental atmospheric processes, especially those related to aerosols, impart our predictive capabilities for future environmental development. In this seminar, the atmospheric formation, chemical aging, cloud processing and fate of aerosol particles are of particular interest, because at present we are still far from an understanding at the molecular level. This statement holds true not only for experimental laboratory studies but also for fundamental process modeling. One aim of the seminar is to foster international collaboration between researchers pursuing fundamental process modeling and those performing laboratory experiments, thus leading to significant improvements in reducing uncertainties in a key component of the atmospheric system needed to understand Earth's complex climate system.

Scientific Organizers:

Prof. Dr. Thomas Leisner
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Program

Program

Sunday, August 26, 2018

17:00 – 21:00	Registration
from 18:30	*BUFFET SUPPER / Informal get together*

Monday, August 27, 2018

07:30	*BREAKFAST*	
08:45 – 09:00	Scientific organizers	**Opening and welcome**

Aerosol Physical Chemistry (APC)

09:00 – 09:40	Christian George	**Photosensitized reactions at the air/water interface**
09:40 – 10:20	Kevin Wilson	**The Interfacial Chemistry of Organic Aerosols and Cloud Droplets**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:30	Allan Bertram	**Diffusion coefficients in organic-water matrices and comparison with Stokes-Einstein predictions**
11:30 – 12:10	Margaret Tolbert	**Looking for Water on Mars: One Drop at a Time**
12:10 – 12:20	**Conference Photo**	
12:20	*LUNCH*	
13:40 – 14:10	**General Discussion APC**	

Program

Monday, August 27, 2018

Aerosol Nucleation (Nuc)

14:10 – 14:50	Jasper Kirkby	**New insights from CLOUD on biogenic new particle formation in pristine to polluted environments**
14:50 – 15:30	Joachim Curtius	**Aerosol formation in the Amazon region: From the Boundary Layer to deep convective outflow - Molecular insights from the CLOUD experiment**
15:30 – 16:10	Hanna Vehkamäki	**Model and experiments to characterise cluster fragmentation inside an Atmospheric Pressure interface Time Of Flight (APi-TOF) mass spectrometer**
16:10 – 16:40	*COFFEE BREAK*	
16:40 – 17:20	Christopher Johnson	**Disentangling the Roles of Structure, Composition, and Intermolecular Interactions in New Particle Formation**
17:20 – 18:00	**General Discussion Nuc**	
18:30	*DINNER*	

Program

Tuesday, August 28, 2018

08:00	*BREAKFAST*	

Aerosols as Ice Nucleating Particles (Ice)

09:00 – 09:40	Angelos Michaelides	**Cold water and ice: Molecular level insight from computer simulations**
09:40 – 10:20	Claudia Marcolli	**Ice nucleation: thermodynamic vs. molecular control**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:30	Alexei Kiselev	**To freeze or not to freeze: competition between dynamic wetting and heterogeneous freezing in supercooled water droplet**
11:30 – 12:10	Barbara Wyslouzil	**Ice nucleation at the edge of no-man's land**
12:10	*LUNCH*	
13:40 – 14:10	**General Discussion Ice**	
14:10 – 14:30	Peter Alpert	**Direct Imaging of Molecular Diffusion and Reaction in Aerosol Particles**
14:30 – 14:50	Cari Dutcher	**Using Microfluidic to Study Thermodynamics and Phase of Single Aqueous Aerosol Droplets**
14:50 – 15:10	Tillmann Buttersack	**On the freezing behavior of small supercooled and hypercooled water droplets**
15:10 – 15:30	Monica Passananti	**Key components in new particle formation: sulfuric acid clusters with guanidine and diamines**
15:30 – 15:50	Tim Esser	**A High Resolution Cryogenic Single Nanoparticle Mass Spectrometer**
15:50 – 16:10	Mario Nachbar	**Heterogeneous ice cloud formation at extreme conditions**

Tuesday, August 28, 2018

16:10	*COFFEE BREAK*
16:40 – 18:00	**Poster Session 1: Experimental Topics**
18:30 – 20:00	*DINNER*
20:00 – 21:30	**Poster Session 1 continued**

Wednesday, August 29, 2018

08:00	*BREAKFAST*	

Aerosol optics (Opt)

09:00 – 09:40	Yinon Rudich	**Relationships between molecular composition change and organic aerosol optical properties**
09:40 – 10:20	Ruth Signorell	**Multistep processes during efflorescence/deliquescence of single, optically trapped aerosol particles**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:30	Jean-Pierre Wolf	**Nucleation and Dissipation of Fog with Ultrashot Lasers**
11:30 – 12:10	Jonathan Reid	**The Evolving Optical Properties of Organic Aerosol Particles**
12:10	*LUNCH*	
13:40 – 14:10	**General Discussion Opt**	
14:10 – 18:00	**Excursion**	
19:00	*HERAEUS DINNER at the Physikzentrum (cold & warm buffet, free beverages)*	

Program

Thursday, August 30, 2018

08:00	*BREAKFAST*	

Fundamentals of Secondary Organic Aerosols (SOA)

09:00 – 09:40	Andrew Ault	**Modification of Aerosol Phase, Acidity, and Structure by Heterogeneous and Multiphase Chemistry**
09:40 – 10:20	Thomas Berkemeier	**Formation and evaporation of organic aerosol from a kinetic modeling perspective**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:30	Hartmut Herrmann	**Multiphase Chemistry Contributions to SOA Formation**
11:30 – 12:10	**General Discussion SOA**	
12:10	*LUNCH*	
13:40 – 14:00	Theo Kurtén	**Computational insights into formation mechanisms and properties of atmospheric autoxidation products**
14:00 – 14:20	Andreas Zuend	**Development of a predictive aerosol viscosity model**
14:20 – 14:40	Josip Lovric	**Water interactions with an organic nopinone surface: a combined theoretical and experimental study**
14:40 – 15:00	Bingbing Wang	**Micro-spectroscopic characterization of particles generated from mesocosm and collected over South China Sea**
15:00 – 15:20	Antoine Roose	**Experimental and theoretical investigation of HO_2 sticking on dicarboxylic acid aerosols**

Program

Thursday, August 30, 2018

Emerging Technologies for Determination of Molecular Structure (ETech)

15:30 – 16:10	Christian Pfrang	**Small-angle X-ray scattering of self-assembled lyotropic phases in single aerosol particles**
16:10 – 16:40	*COFFEE BREAK*	
16:40 – 18:00	**Poster Session 2 : Theoretical Topics**	
18:30 – 20:00	*DINNER*	
20:00 – 21:30	**Poster Session 2 : continued**	

Friday, August 31, 2018

08:00	*BREAKFAST*	

Emerging Technologies for Determination of Molecular Structure (ETech)

09:00 – 09:40	Nønne Prisle	**Exploring the potential for synchrotron radiation based methods to study organic aerosol-water interactions directly at the molecular level**
09:40 – 10:20	Markus Amman	**Perspective of X-ray excited electron spectroscopy to probe chemistry and structure at the surface of aerosol proxies**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:30	Michael Fárnik	**Uptake of atmospheric molecules on acid clusters**
11:30 – 12:10	**General Discussion ETech**	
12:10	*LUNCH*	
13:40 – 14:10	Scientific organizers	**Poster Awards** **and** **Final / General Discussion**

End of the seminar** and **Departure

*Please note that there will be **no** dinner at the Physikzentrum on Friday evening for participants leaving the next morning.*

Posters

Posters

1	Ahmed Abdelmonem	**Application of Nonlinear Optical Spectroscopy in Molecular Level Characterization of Atmospheric Aerosol-Water Interactions**
2	Peter Alpert	**Iron Oxidation as a Tracer for Radical Reactions Inside Organic Aerosol Particles**
3	Nir Bluvshtein	**Towards using the photophoresis for measurements of light absorption by a single particle**
4	Tillmann Buttersack	**Hypercooled water**
5	Bryan Bzdek	**Measurements and modelling of surfactant coated aerosol particles**
6	Man Nin Chan	**Chemical Transformation of Organosulfates through Heterogeneous OH Oxidation: Formation of Inorganic Sulfate and Sulfate Radical Anion Chemistry**
7	Michael Cotterell	**Aerosol Optical Properties during Homogenous and Heterogeneous Brown Carbon Formation**
8	Grégory David	**Digital holography of optically-trapped aerosol particles**
9	Matus Diveky	**Single Droplet Photoacoustic Spectroscopy**
10	Jing Dou	**Iron Reoxidation in Photochemical Cycling**
11	Jonas Elm	**Towards Modelling the Catalytic Effect of Atmospheric Molecular Clusters**
12	Peter Gallimore	**Single particle spectroscopy: 1064 nm Raman and the use of probe molecules**

Posters

13	Benjamin Hoffman	**A High Resolution Cryogenic Single Nanoparticle Mass Spectrometer**
14	Frances Houle	**Computational prediction of the chemical signatures of autoxidation of organic aerosol under atmospheric conditions**
15	Alice Keinert	**Heterogeneous freezing on thin sections of K-feldspar: active sites vs. Surface chemistry**
16	Ulrich Krieger	**SERS pH nanoprobes in single, levitated aerosols particles**
17	Thomas Leisner	**The volatility of ice below 160K**
18	Mario Nachbar	**Heterogeneous ice cloud formation at extreme conditions**
19	Matthew Nee	**Modeling photo-oxidation and aerosol uptake of reduced sulfur and nitrogen compounds**
20	Shu-feng Pang	**The reaction between sodium carboxylate and ammonium sulfate in internally mixed aerosols**
21	Evelyne Parmentier	**Photochemistry of single trapped organic aerosol droplets in the submicron size range**
22	Erik Thomson	**Water interactions with organic surfaces: uptake, accommodation, and ice nucleation**
23	Celine Toubin	**Water interactions with organic surfaces insights from environmental molecular beam and molecular dynamics studies**

Posters

24	Huanyu Yang	**Towards the surface science of ice nucleation on aqueous organic solutions and solid substrates**
25	Xiuhui Zhang	**Nucleation mechanism of oxocarboxylic acids involving hydration reaction:Implications for the atmospheric model**

Abstracts of Lectures

(in chronological order)

Photosensitized reactions at the air/water interface

Marie Roveretto, Xinke Wang, Nathalie Hayeck and Christian George

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Surfaces coated with biogenic surfactants exposed to the atmosphere are ubiquitous and are commonly present on aerosol particles, cloud droplets, buildings, plants, and oceans. As shown in the past, photochemical reactions taking places at these air/water interfaces lead to unique chemical pathways, producing volatile organic compounds (VOCs) and leading to secondary organic aerosol formation.

Here, photochemical processes at the air/water interface of fatty acids layer on water containing, or not, various photosensitizers were studied, demonstrating VOC production.

Using a combination of online-APCI-HRMS and PTR-ToF-MS, unsaturated and functionalized VOCs were identified and quantified. We suggested that fatty acids alone at the air water interface do, once irradiated, induce peroxy-radical chemistry. Indeed the presence of these peroxy radicals has now been revealed and quantified by interfacial chemical titration. In addition, the photochemical lifetime of such fatty acids on water has now been investigated by means of Langmuir through.

Moreover, for solutions containing a photosensitizer and various inorganic salts, we observed in addition the emissions of various oxidants. For instance, for water mimicking salty water, various halogenated products and radicals have been observed by means of an online-APCI-HRMS. While in presence of nitrate anion, HONO formation seems to dominate.

This presentation will present and discuss these finding, highlighting how photosensitizing may influence condensed phase chemistry in the troposphere.

The Interfacial Chemistry of Organic Aerosols and Cloud Droplets

Kevin R. Wilson

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA USA. krwilson@lbl.gov

Developing accurate descriptions of how interfaces control the multiphase chemistry of environmental surfaces remains an outstanding challenge. In particular, it is now well-established that submicron particles (i.e. aerosols) play substantial roles in the chemistry of the troposphere with larger scale impacts on climate and human health. The presence of aerosols increases substantially the microphysical complexity needed to accurately model the chemical evolution of current and future atmospheres. This complexity is due in large part from the coupling of reaction and diffusion timescales, which can be largely ignored in reaction networks of isolated gas phase molecules. However, this is not the case, when multistep reaction mechanisms occur across an interface between gas and condensed phases. Using a number of model systems, we examine multiphase chemistry of free radicals and Criegee intermediates in an effort to develop a microscopic understanding of the interplay between molecular reactivity, transport, hygroscopic growth and chemical erosion at model aerosol surfaces. In related work we have examined the importance of interfacial chemistry on cloud formation on aerosols. For realistic mixed inorganic/organic aerosols, the cloud droplet size at activation is much larger than what would be predicted based upon bulk solubility alone and points to the important and often subtle role that interfacial organic molecules play in the cloud droplet formation mechanism.

Diffusion coefficients in organic-water matrices and comparison with Stokes-Einstein predictions

E. Evoy[1], A. Maclean[1], S. Kamal[1], and A. K. Bertram[1]

[1]*University of British Columbia, Vancouver, Canada*

Diffusion coefficients of organic species in particles containing secondary organic material (SOM) are necessary for predicting the growth and reactivity of these particles in the atmosphere, as well as the long-range transport of pollutants. Previously, the Stokes-Einstein equation, combined with viscosity measurements, has been used to predict these diffusion coefficients. However, the accuracy of the Stokes-Einstein equation for predicting diffusion coefficients in SOM-water particles has not been quantified. To test the accuracy of the Stokes-Einstein equation, diffusion coefficients of fluorescent organic probe molecules were measured in a range of proxies for SOM-water particles found in the atmosphere, using fluorescence recovery after photobleaching. Measurements were performed as a function of water activity, ranging from 0.2 to 0.9, and as a function of viscosity, ranging from ~10^{-3} to ~10^{6} Pa s. The measured diffusion coefficients were compared with predictions made using the Stokes-Einstein equation combined with literature viscosity data. Within the uncertainties of the measurements, the measured diffusion coefficients agreed with the predicted diffusion coefficients, up to a viscosity of 10^{3} Pa s. At higher viscosities, breakdown of the Stokes-Einstein equation was observed in some cases. These results will be presented and the implications discussed.

Looking for Water on Mars: One Drop at a Time

M. A. Tolbert, K. Primm, S. B. Ushijima, R. D. Davis and R. V. Gough

University of Colorado, Boulder, USA

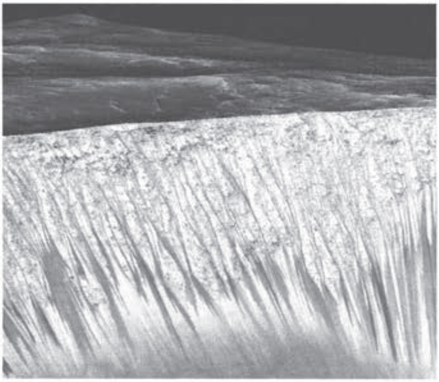

Fig. 1. *"Recurring slope lineae," on Garni Crater of Mars, constructed from observations by the High Resolution Imaging Science Experiment (HiRISE) camera on NASA's Mars Reconnaissance Orbiter. Photo credit: NASA*

Mars is a cold, dry planet where pure liquid water is not stable. However, recent observations of "recurring slope lineae" (RSL) on Mars may be evidence of current liquid water flows. Several different hygroscopic salts are known to exist in the Martian soil, and deliquescence of those salts could provide small amounts of liquid water temporarily. Our research group uses Raman microscopy and an environmental cell to probe the conditions under which droplets of such liquid brines can form and persist under low Martian temperatures. In addition, an optical trap is used to probe phase changes of individual levitated droplets. In addition to homogeneous phase transitions, heterogeneous nucleation is examined in both contact and immersion mode using analogs for the Martian regolith as the nucleating particle. In this talk, I will discuss laboratory results for the brine-forming ability of several different Mars-relevant salts and salt mixtures, brine metastability, and implications for water on Mars.

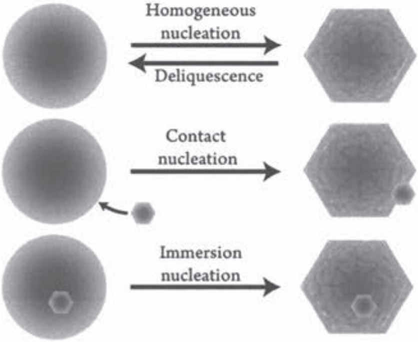

Fig. 2. *Phase transitions of Martian salts, specifically perchlorates and chloride, discussed in this talk. Heterogeneous nuclei include Martian soil simulants.*

References

[1] R.V. Gough et al., Formation of Aqueous Solutions on Mars, EPSL 393, (2014).

[2] S. B. Ushijima et al., Immersion and Contact Efflorescence Induced by Mineral Dust, J. Phys. Chem. A 122, (2018).

New insights from CLOUD on biogenic new particle formation in pristine to polluted environments

Jasper Kirkby[1,2] and the CLOUD collaboration
[1]*Goethe University Frankfurt, 60438 Frankfurt am Main, Germany*
[2] *CERN, CH1211 Geneva, Switzerland*

By current estimates, about half of all cloud condensation nuclei (CCN) originate from the nucleation of trace atmospheric molecules rather than being emitted directly into the atmosphere [1]. Human activities since pre-industrial times have increased atmospheric pollution and, in turn, aerosols and CCN. This has partially offset the warming due to greenhouse gases, although the amount remains poorly understood and constitutes the largest uncertainty in anthropogenic radiative forcing [2].

The CERN CLOUD experiment recently reported that biogenic highly oxygenated molecules (HOMs) produce abundant particles without sulphuric acid [3]. Previously it was thought that sulphuric acid – which largely arises from sulphur dioxide emitted by fossil fuels – was essential to initiate almost all particle formation. This establishes a new paradigm for atmospheric particle nucleation in which biogenic HOMs play a role comparable to sulphuric acid; together with a suitable stabilising agent, each has sufficiently low volatility to form new particles in the lower atmosphere at vapour concentrations near 1 part per trillion by volume (pptv). The new mechanism implies the presence of a ubiquitous source of biogenically-driven aerosols alongside the largely anthropogenically-driven aerosols with sulphuric acid. Pure biogenic nucleation raises the baseline aerosol state of the pristine pre-industrial atmosphere, thereby reducing estimates of anthropogenic radiative forcing [1].

The discovery of pure biogenic nucleation involved ozonolysis of alpha-pinene at a single temperature [3]. During the last two years, CLOUD has extended the measurements to investigate biogenic NPF and early growth under realistic atmospheric conditions between pristine and polluted environments. The experiments involved single- to multi-component mixtures of several biogenic vapours, NOx, sulphuric acid and ammonia, and were carried out at various temperatures between the tropical boundary layer (25°C) and upper free troposphere (-50°C). The new insights from CLOUD on biogenic NPF will be discussed in this and the following presentation (J. Curtius).

References

[1] Gordon, H., *et al. (CLOUD),* PNAS **113**, 12053-12058 (2016).
[2] Myhre, G., *et al.,* IPCC 5th Assessment Report, Cambridge Univ. Press (2013).
[3] Kirkby, J. *et al. (CLOUD),* Nature **533**, 521-526 (2016).

Aerosol formation in the Amazon region: From the Boundary Layer to deep convective outflow - Molecular insights from the CLOUD experiment

J. Curtius[1]

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Recent laboratory investigations from the CLOUD experiment at CERN revealed efficient nucleation [1] and early growth [2] of aerosol particles from Highly Oxygenated Organic Molecules (HOMs) formed from ozonolysis of biogenic VOCs such as α-pinene. Based on these laboratory results it would be conceivable that such pure biogenic nucleation processes could also occur frequently in the Boundary Layer of the Amazon Basin [3] but field observations show that aerosol nucleation is rare under these conditions [4] while strong nucleation events and efficient growth are found to occur in the aged outflow of deep convection high above the Amazon [5]. Here we present a series of dedicated CLOUD measurements to investigate the influence of a) temperature, b) isoprene, c) NO_x, d) UV photolysis, e) ion concentration, and f) condensation sink on either boosting or suppressing aerosol nucleation of HOMs from α-pinene. The radical chemistry and the molecular steps leading to HOMs and HOM-dimers that are suitable – or not suitable – to form new particles are elucidated.

References

[1] J. Kirkby et al., Nature, **533**, 521-527 (2016).
[2] J. Tröstl et al., Nature, **533**, 527-531 (2016).
[3] H. Gordon et al., PNAS, **113**, 12053-12058 (2016).
[4] S.T. Martin et al., Rev. Geophys., **48**, 2008RG000280 (2010).
[5] M.O. Andreae et al., ACP, **18**, 921-961 (2018).

Model and experiments to characterise cluster fragmentation inside an Atmospheric Pressure interface Time of Flight (APi-ToF) mass spectrometer

M. Passananti[1], E. Zapadinsky[1], J. Kangasluoma[1], N. Myllys[1], T. Zanca[1], M. Attoui[2], H. Vehkamäki[1]

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Mass Spectrometers (MS) such as the Atmospheric Pressure interface Time Of Flight (APi-TOF) and the Chemical Ionization APi-TOF (CI-APi-TOF) are able to detect molecules and small clusters, which are involved in the first stages of new particle formation, even at environmental low concentration [1]. Correct accounting of collision induced cluster fragmentation [2] is however of vital importance for retrieving the initial cluster distribution in the experiments. Therefore, we are performing a systematic experimental study on the fate of clusters inside the APi-TOF and developing a model to predict the fragmentation of clusters inside the mass spectrometer.

We produced negatively charged sulphuric acid clusters by ElectroSpray Ionization and selected three acid clusters using a Differential Mobility Analyser (DMA) to inject into the APi-TOF. We studied fragmentation inside the APi, consisting of three vacuum chambers where an electric field is applied to guide the ions through the interface. We evaluated the effects of the voltages applied to the electrodes in the three chambers without changing the radio frequencies.

We also developed a model for the cluster fragmentation inside the APi. In this model, the charged clusters move through the APi under applied constant and uniform electrical field (defined by the tuning of the instrument). The fate of cluster is simulated as a random process involving collisions with carrier gas, energy transfer and fragmentation.

Both experiments and simulations indicate clusters are mainly fragmented at the interface between the first and second chamber, and the model captures the observed extent of fragmentation. The development of this model and its validation by laboratory experiments is crucial to correctly interpret the experimental data obtained by APi-TOF instruments.

References

[1] A. Kürten, PNAS **111**, 15019- 15024 (2014)
[2] F.D. Lopez-Hilfiker, Atmos. Meas. Tech. **9**, 1505-1512 (2016)

Disentangling the Roles of Structure, Composition, and Intermolecular Interactions in New Particle Formation

Christopher J. Johnson, **Sarah E. Waller**, **Yi Yang**, **John J. Kreinbihl**

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As a result of extensive study, a mechanism describing new particle formation (NPF) in the atmosphere is beginning to emerge. However, role of intermolecular interactions such as proton transfer and hydrogen bonding in governing particle formation and growth have proven difficult to quantify. Our group has been using vibrational spectroscopy and temperature-controlled ion trap mass spectrometry to evaluate the structures, energetics, and growth of clusters of sulfuric acid with ammonia and amines. For small clusters with fewer than ten molecules, we find that hydrogen bonding interactions can actually compete with Coulombic interactions between conjugate acid and base ions in determining the cluster structure.[1] In an extreme example, substitution of trimethylamine for ammonia forces direct hydrogen bonding between bisulfate anions. We have developed a simple and general model to predict when these rearrangements must be found in clusters.

We have also examined the hydration of these clusters, an elusive factor in the overall NPF mechanism due to difficulties in unambiguously detecting hydration using sampling techniques. The extent of hydration is found to vary inversely with the number of amines in the cluster for all cases studied. Further, by comparing amines with the same hydrogen bonding arrangement but differing basicity, we have shown that the uptake of water correlates strongly to the number of hydrogen bond donors on the surface of the cluster, and more weakly with the net basicity of the cluster. In fact, the correlation with basicity is no stronger than the correlation *between* basicity and number of hydrogen bond donors. This suggests that, at least for small cluster sizes, structure is the dominant factor in determining hydration, and that earlier results indicating a role of cluster acidity arise from the correlation between basicity and structure.[2]

References

[1] S. E. Waller, Y. Yang, E. Castracane, E. E. Racow, J. J. Kreinbihl, K. A. Nickson, and C. J. Johnson, J. Phys. Chem. Lett. **9**, 1216-1222 (2018)

[2] J. M. Thomas, S. He, C. Larriba-Andaluz, J. W. DePalma, M. V. Johnston, and C. J. Hogan, Phys. Chem. Chem. Phys **18**, 22952 (2016)

Cold water and ice: Molecular level insight from computer simulations

Angelos Michaelides[1]

[1]*University College London, UK*

Recent work from our research group in which we are trying to understand the intimate molecular level details of water freezing will be discussed. A particular emphasis will be placed on the role the surfaces of foreign materials play in accelerating the nucleation process [1-4] and on the dynamical nature of the nucleation event.

References

1. M. Fitzner, G. C. Sosso, S. J. Cox and A. Michaelides, J. Am. Chem. Soc. **137**, 13658 (2015)
2. G. Sosso et al., J. Phys. Chem. Lett. **7**, 2350 (2015)
3. A. Kiselev et al, Science **355**, 367 (2017)
4. M. Fitzner et al., Nature Comm. **8**, 2257 (2017)

Ice nucleation: thermodynamic vs. molecular control

C. Marcolli

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Ice nucleation in the atmosphere leads to cloud glaciation and precipitation. Classical nucleation theory describes homogeneous ice nucleation as an activated process. Once the ice embryo has reached critical size, the energy invested to increase the interface between the embryo and liquid water starts to exceed the energy gain due to the incorporation of further water molecules into the ice lattice. The energy barrier to ice nucleation is reduced when the ice embryo forms on a foreign surface which decreases the energy requested to build up the interface.

In 2000, Koop et al. [1] showed that homogeneous ice nucleation in solution droplets can be described as a function of water activity without having to consider the specific properties of the solutes. Surprisingly, also for heterogeneous ice nucleation numerous systems showed a dependence on water activity only, indicating a lack of specific interactions between the ice nucleating surface and the solutes [2] and pointing to a thermodynamic control of heterogeneous ice nucleation as well.

However, recent studies with feldspars show relevant deviations from this simple thermodynamic description due to interactions of the feldspar surface with water and solute species such as ion exchange, surface adsorption and slow dissolution of the mineral surface [3]. There is convincing evidence that ice nucleation does not occur with a uniform rate on the whole surface of ice nucleating particles, but on special sites with exceptionally high nucleation rates [4]. While these sites seem to be related to the regular surface properties, insight into the special molecular makeup that singles them out as ice nucleation active is still lacking.

Pressure influences ice nucleation in a similar way as water activity suggesting a thermodynamic control. Liquids can attain negative pressures when they are stretched. While pressurizing water leads to a freezing point depression, negative pressure should increase the freezing temperature. However at negative pressures, ice nucleation is in competition with bubble nucleation [5]. I will explore scenarios where ice nucleation may be triggered by negative pressure.

References

[1] T. Koop et al., Nature **406**, 611 (2000)
[2] B. Zobrist et al., J. Phys. Chem. A **112**, 3965 (2008)
[3] A. Kumar et al., Atmos. Chem. Phys. 18, 7057 (2018)
[4] L. Kaufmann et al., Atmos. Chem. Phys. **17**, 3525 (2017)
[5] C. Marcolli, Sci. Rep. **7**, 16634 (2017)

To freeze or not to freeze: competition between dynamic wetting and heterogeneous freezing in supercooled water droplet

Alexei Kiselev[1], Nadine Tüllmann[1], Michael Koch[1], Alice Keinert[1], and Thomas Leisner[1,2]

1) Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

2) Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany

Freezing of supercooled water in contact with a foreign substrate can be facilitated by the presence of special surface sites assisting the formation of a critical ice embryo. Under stationary conditions, the probability of freezing can be described by the Classical Nucleation Theory with account for the properties of such sites and stochastic nature of nucleation. Recent progress in atomistic modeling and experimental research allowed for a significant improvement in the quantitative description of heterogeneous ice nucleation.

However, the freezing mechanism becomes more complicated under non-equilibrium conditions, for example, if a supercooled droplet experiences a collision with an ice nucleating particle or substrate. Depending on the wetting behavior of the substrate and temperature, a droplet would require some time to achieve a stable equilibrium on the substrate. During this transition, freezing kinetics can be influenced by changing properties of the water-substrate interface.

In this contribution, we report experimental measurements of supercooled droplets freezing upon contact with the precooled surfaces of freshly cleaved feldspar, graphite, silicon, and ice. We explore the competition between dynamic wetting and freezing by recording the freezing-upon-collision events with a high-speed video camera (see Figure 1). We report the measurements of the average time needed to initiate freezing for different types of IN particles and substrates. Surprisingly, this characteristic time delay does not correlate with the efficacy of the ice nucleating substrate, nor does it show a strong correlation with the area of the water-substrate interface. Finally, we discuss possible mechanisms of such freezing behavior and potential implications for the future ice nucleation research.

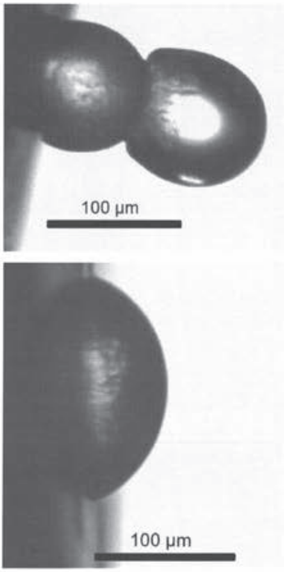

Figure 1. Droplet freezing upon collision with ice (above) and mineral surface (below).

Ice nucleation at the edge of no-man's land

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Accurate measurements of ice nucleation rates, and the phase or structure of the particles formed, are critical for developing reliable models of climate and atmospheric chemistry, as well as testing our understanding of the behavior of water under extreme conditions. Experiments using micron size droplets cannot, generally, measure ice nucleation rates below ~235 K and, thus, this temperature often defines one edge of no-man's land for supercooled water. Extensive ice nucleation rate measurements made slightly above 235 K agree quite well with each other in spite of their extreme temperature sensitivity. At much lower temperatures (180 – 212 K), well within no-man's land, rate measurements can be made in nanodroplets, and in this regime rates also agree well and are extremely insensitive to temperature. Nucleation rates measured at intermediate temperatures, ~212 K $\leq T_d \leq$ ~235 K, are more controversial with rates reported near 228 K differing by ~6 orders of magnitude.

This talk will summarize our recent work [1, 2, 3] that focuses on further exploring ice nucleation in this intermediate temperature regime in order to fill in the rate gap between nano- and micro-droplets. Particles are formed via condensation in supersonic nozzles and the system is characterized using a range of in situ techniques including small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), infrared spectroscopy, and pressure measurements. We attempt to correct classical nucleation theory by adjusting the physical properties of water for the increasing internal pressure as the droplets decrease in size.

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Direct Imaging of Molecular Diffusion and Reaction in Aerosol Particles

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Organic aerosol particles at low relative humidity, *RH*, and temperature, *T*, can be semi-solid or glass-like having a viscosity $<10^{12}$ Pa s which has been previously shown to limit molecular diffusion. However at a *T* and *RH* typical for the Earth's surface, small molecules such as H_2O can equilibrate quickly in concentration throughout the bulk of ambient organic particles. In contrast, molecules in photoactive particles or particles exposed to oxidizing trace gasses not only undergo diffusion, but also reaction. Together, diffusion and reaction may result in a non-equilibrium state characterized by radial concentration gradients within particles despite quick equilibrium timescales based on diffusion alone. Although suggested or predicted in previous studies, direct observation of concentration gradients in a reactive aerosol system has not been achieved. We used UV light (370 nm at 3 W m^{-2}) to photochemically react submicrometer sized aerosol particles containing Fe(III)-citrate and citric acid with a 1:1 mole ratio in the presence of O_2 and quantified Fe oxidation state using scanning transmission X-ray microscopy coupled with near-edge X-ray absorption fine structure (STXM/NEXAFS) spectroscopy at the Swiss synchrotron light source. Resonate absorption peaks corresponding to Fe(II) and Fe(III) allowed quantification of Fe photochemical reduction or reoxidation as a function of time after UV irradiation ceased. Fe(III) fraction, β, over single particles was imaged with a pixel resolution of 35 x 35 nm. Immediately after UV irradiation stopped, particles were reduced with $\beta \approx 0.2$. Over time, β values in single particles remained the same for *RH*=0 and 20% and tended to increase for *RH*=40 and 60% over hour timescales. However, we observed that particle surfaces reoxidized faster than particle cores. This can only be explained by a lack of O_2 in particle cores to generate the reactive oxygen species (ROS) needed to react Fe(II) to Fe(III). Without ROS, we hypothesize that free organic radicals (FR) produced due to decarboxylation reactions subsequent of ligand-to-metal charge transfer should be preserved. The low molecular self-diffusion of the organic matrix and O_2 uptake and reaction should also be restricted at particle surface layers. A newly developed physiochemical reaction and kinetic model was developed and constrained with our STXM data to derive ROS and FR concentrations under atmospheric conditions. We identified RH and T regimes in which ROS and FR concentration reach maximum and minimum values in particles, entirely dependent on reaction and molecular diffusion time scales.

Using Microfluidic to Study Thermodynamics and Phase of Single Aqueous Aerosol Droplets

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Measurements of phase and phase change events in chemically complex aqueous droplets provide valuable information for understanding the dynamic processes in these complex micro-environments. For example, atmospheric aerosol droplets regularly undergo phase changes including liquid-liquid phase separation and crystallization. The phase and mixing state of the aerosol has profound effects on particle morphology, species uptake, equilibrium partitioning, activation to cloud condensation or ice nuclei, and optical properties. Many factors play a role in determining if a droplet will liquid-liquid phase separate, as well as its resulting orientation or morphology of the two phases, such as temperature, relative humidity, and chemical composition of the respective phases. In this work, single atmospheric aerosol droplet chemical mimics are generated in microfluidic channels and stored in passive traps until dehydration to study the influence of relative humidity and water loss on phase behavior. The solution volume of the droplet trapped changes with respect to time, and is calculated by image analysis and correlated with the concentration of the solution to determine water activities at each time interval.[1] The research will help determine mixture liquid-liquid phase separation and efflorescence events of droplets that include presence of other dissolved components and tend to decrease the water activity. The measurements will also be used to parameterize statistical thermodynamic modeling for predictions of thermodynamic properties of aqueous aerosols as a function of relative humidity.

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On the freezing behavior of small supercooled and hypercooled water droplets

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For deeply supercooled liquids the transition from a two-stage freezing process [1] to complete solidification in just one freezing step occurs at the hypercooling temperature, a term that seems to be almost unknown in water research; to our knowledge, it has only been mentioned by Dolan et al. for high-pressure ice [2]. The reason for the absence of this expression may be that the best estimate to be found in the literature for the hypercooling temperature of water is about −160°C (113 K) [3]. This temperature is far below the limit of experimentally realizable degrees of supercooling near −40°C (233 K), which marks the homogeneous nucleation temperature T_H of common pure water; in fact, it is even below the glass-transition temperature (133 K). We show that, surprisingly, a more thorough analysis taking into account the temperature dependence of the heat capacities of water and ice as well as of the enthalpy of freezing shows that the hypercooling temperature of water is about −64 °C or 209 K, almost 100 K higher than estimated before [4]. One of the most exciting consequences is that existing experiments are already able to reach these degrees of supercooling, and it is our prediction that a transition in the freezing behavior occurs at these temperatures. We further present experimentally and theoretical results on the distribution of ice portions and temperature (FEM simulation) of freezing supercooled water (micro) droplets considering the heat transfer via the drop surface [5]. Here the critical radius towards one-step freezing was found to be in the range of 0.1 to 1 μm for supercoolings of 25 K.

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Key components in new particle formation: sulfuric acid clusters with guanidine and diamines

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New particle formation in the atmosphere is an important process that can influence the climate, indeed it has been estimated that 45% of the global cloud condensation nuclei are derived from nucleation [1]. Sulfuric acid is believed to be a common precursor enforcing new particle formation in many inland environments, but another stabilizing vapor is required to explain new particle formation events observed in the atmosphere. It has been shown that homogeneous nucleation involving ammonia and sulfuric acid cannot explain the nucleation rates and growth rates observed in the atmosphere and that nucleation involving dimethylamine and sulfuric acid could explain only some observed ambient nucleation rates [1]. More than 150 amines have been detected in the atmosphere [2], these amines could interact with sulfuric acid and the interaction strength depends on their structure and basicity.

We have investigated, experimentally and through computational methods, the stability of sulfuric acid clusters with diamines (cadaverine and putrescine) and with guanidine, a proxy for strong organobases. Recent measurements have indicated that diamines (putrescine and cadavarine) are omnipresent in the ambient atmosphere and in some cases can reach the concentration of monoamines [3].

We observed for all the studied organobases that they form strong clusters with sulfuric acid and using the Atmospheric Cluster Dynamics Code (ACDC) [4] we evaluated the cluster kinetics observing a significant increase of growth rate compared to sulfuric acid dimethylamine clusters.

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A High Resolution Cryogenic Single Nanoparticle Mass Spectrometer

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Diverse nanoparticles, originating from natural or anthropogenic sources, exist in the atmosphere where they directly, through scattering and absorbing of sunlight, and indirectly, by serving as cloud condensation nuclei (CCN), affect the climate. Especially their ability to act as CCN is an important but not well understood aspect of cloud model simulations. Since clouds cover roughly two thirds of the globe they play a striking role in simulations of world's climate but their formation mechanism still remains one of the greatest uncertainties. To improve the quality of such simulations the nanoparticle properties, e.g. surface structure and reactive behaviour, have to be characterised experimentally.[1,2]

Motivated by the work of the groups of Gerlich and Anderson[3-5] we developed a cryogenic, single nanoparticle mass spectrometer to investigate the surface structure and reactive behaviour of a broad range of nanoparticles in the size range of 5 to 50 nm. A single nanoparticle from a nanospray ion source is trapped in a custom-designed quadrupole ion trap which is mounted on the second cooling stage of a closed-cycle Helium cryostat. The particles mass-to-charge ratio m/z is accurately measured by optically monitoring the particles secular oscillation frequency. This enables us to monitor m/z variations of a single nanoparticle, depending on temperature (10-350 K), background gas and interaction with light over several days.

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Heterogeneous ice cloud formation at extreme conditions

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Heterogeneous ice cloud formation at extreme cold temperatures below 150K can be encountered in planetary atmospheres, e.g. polar mesospheric clouds on Earth or water ice clouds on Mars. In the case of polar mesospheric clouds on Earth, ice nucleation is activated on sub 2nm meteoric smoke particles. The formation process of ice clouds at such cold temperatures on nanometer sized nuclei is not well understood because no ice nucleation experiments for such conditions existed so far. In this contribution, we present results from a laboratory experiment which is designed to study ice nucleation processes below 150K on nanoparticles on a microphysical scale.

We determine the binding energy/desorption energy of water molecules on the particle material, which allows us to parameterize the amount of water molecules which are adsorbed on a surface as function of temperature and saturation. In addition, we are able to evaluate for the temperature dependent sublimation flux of water molecules from the phase growing on the particles and conclude that the deposited ice polymorph below 150K is amorphous solid water (ASW). We show that the saturation vapor pressure of ASW is higher than previously assumed which significantly affects the ice growth behavior of the particles. We present a new parameterization for the saturation vapor pressure of ASW. Finally, we determine critical saturations for the onset of ice growth and present a method to predict critical saturations needed for cloud formation below 150K. Moreover, we will discuss the influence of the particle charge on the ice formation process.

Relationships between molecular composition change and organic aerosol optical properties

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The wavelength-dependence of the complex refractive indices (RI) in the visible spectral range of secondary organic aerosols (SOA) and of biomass burning aerosol, and the evolution of the RI with atmospheric aging are largely unknown. In this study, we apply a novel white light-broadband cavity enhanced spectroscopy to measure the changes in the RI (365−650 nm) of biogenic and anthropogenic SOA produced and aged in an oxidation flow reactor, simulating daytime aging under different NOx concentrations. In addition, we use novel new tar balls proxy to study the effect of atmospheric aging on the optical properties of biomass burning aerosols. Correlating the observed optical properties with aerosol mass spectrometer measurements allows to correlate changes in the chemical composition of the aerosols and their optical properties.

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Multistep processes during efflorescence/deliquescence of single, optically trapped aerosol particles

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Particle shape, size, refractive index, and chemical composition are key properties that govern the interaction of aerosols with light and the surrounding atmosphere. Single particle measurements allow detailed studies of how these properties are affecting and are affected by atmospheric processes such as evaporation, hygroscopic growth, phase transitions and photochemistry. The behavior of submicron-sized particles is especially interesting due to their enhanced aging kinetics compared with micron-sized particles. In this contribution, we report measurements of the dynamics of single, optically-trapped, submicron and micron-sized particles while mimicking these atmospheric processes. We use counter-propagating optical tweezers (CPT) to isolate a single particle in air and combine UV broadband light-scattering (BLS) measurements with Raman spectroscopy to characterize the time evolution of particle size, refractive index, and chemical composition. Fast BLS measurements (10 ms time resolution) showed that complex multiple processes occur during the efflorescence and deliquescence of aqueous K_2CO_3 particles isolated in air. The efflorescence occurs either in a single process within less than 10 ms or through a multistep process that can last more than 10 s, while the deliquescence occurs through multistep processes only. BLS measurements allow us to observe these multistep phase transitions qualitatively, but in general they cannot quantify the shape and size of the particles when these are nonspherical (e.g. during and after the efflorescence or before and during the deliquescence). We are currently developing a high spatial and temporal resolution (770 nm and 240 µs respectively) holographic imaging approach to quantify the dynamics of the particle shape during these multistep phase transitions. The first results from this holographic imaging will be presented.

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Nucleation and Dissipation of Fog with Ultrashort Lasers

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Ultrashort and intense lasers propagating in air undergo filamentation, a self-sustained nonlinear propagation mode, which leads to high intensity light strings spanning over very long distance in air [1]. This allows nonlinear photo-chemical processes to occur in air, which leads to aerosol nucleation and water condensation [1-4]. In the near-infrared (NIR), both laboratory and field studies have shown that the major pathway for laser-induced condensation is associated with the local formation of HNO_3 in the atmosphere for relative humidity (RH) as low as 70%. Furthermore, NIR laser pulses oxidize volatile organic compounds (VOCs) much faster than in the natural atmosphere, resulting in fast ageing and increased condensability [4]. On the other hand, Mid-IR lasers have recently emerged as very attractive sources for atmospheric applications, since they potentially allow kilometer long filaments bearing even higher intensities. For atmospheric water condensation, however, the higher order of the non-linear processes was expected to reduce drastically the yield. We show for the first time that mid-IR filaments at 3.9 um are surprisingly able to produce as many aerosols particles as 100 mJ-1J class lasers at 800 nm. The mechanism behind this amazing efficiency relies on a completely different pathway (resonant condensation) as the "nitrogen route" highlighted above.

Laser filaments also produce mechanical effects in the atmosphere. We present here recent results that demonstrate that the mechanical shockwave can be used to cut a path through fog [5]. More precisely, by using high repetition rate ultrashort lasers, droplets from an artificial dense fog are expelled from the center, increasing the transmission through it from 0% to 30 %. The energy required for moving the droplets away from the central beam is much lower than the energy needed to vaporize them. These experiments open new perspectives to overcome the interruption of laser data transmission due to fog in classical and quantum free space optical telecommunications.

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The Evolving Optical Properties of Organic Aerosol Particles

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Secondary Organic Aerosols (SOA) formed from the atmospheric processing of volatile organic components (VOCs) can account for a substantial fraction of the total ambient aerosol mass. Our understanding of the impact of SOA on atmospheric processes, such as cloud droplet formation and the interaction with solar radiation, can greatly benefit from an accurate characterisation of the physicochemical properties of the SOA and the dynamical processes that lead to their variation. Here, we will present a single particle approach [1] to explore the factors that govern the optical cross-sections of SOA particles, the variation with the precursor VOC, and the dependence on the dominant chemical components.

SOA samples are generated in a photo-chemical flow reactor from the oxidation of a VOCs precursor, such as α-pinene and toluene, with known VOC, NOx and ozone concentrations, and collected with an electrical low pressure impactor. Single charged SOA solution droplets generated from these samples are confined within an Electrodynamic Balance in a gas flow with controlled temperature and relative humidity (RH). Each single confined droplet is illuminated by laser light (532 nm) and the resulting light scattering pattern (or optical extinction cross-section) is measured and fitted to monitor the evolving radius and the refractive index (RI) of the droplet when exposed *in situ* to changes in gas phase composition, temperature and RH.

We will report measurements of particle RI and the processes that lead to a change in RI for SOA samples formed from four different VOC precursors. More specifically, we will explore the dependence of the optical growth factor on equilibrium hygroscopic response over a wide range in RH (<5 % to >99.5 %). The dependence of the optical properties on the volatility distribution of semi-volatile organic components (SVOCs) present within the condensed phase will also be examined. Kinetic factors regulating gas-particle partitioning of water and SVOCs, and the consequences for the optical cross section, will also be reported over a temperature range extending from 255 to 320 K.

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Modification of Aerosol Phase, Acidity, and Structure by Heterogeneous and Multiphase Chemistry

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Secondary organic aerosol (SOA) is a ubiquitous component of submicron ambient aerosol, but its formation mechanisms and the connection between chemical composition and physical properties are not well understood. In recent years, aerosol phase has been shown to range from to solid to semi-solid to liquid for ambient particles, Morphology (e.g. core-shell) of SOA with inorganic components (e.g. ammonium sulfate) have shown morphologies ranging from well-mixed liquid particles to core shell or more complex morphologies as a function of relative humidity (RH) and temperature. The changing water content of aerosols can impact acidity and reactive uptake of molecules such as isoprene epoxydiols (IEPOX). However, direct evidence of the impact of non-liquid phases and phase separation on heterogeneous uptake and continuing chemistry in aerosols is far more limited. Herein, we use atomic force microscopy (AFM) with phase images and photothermal infrared spectroscopy (AFM-PTIR), electron microscopy, and Raman microspectroscopy to probe phase, structure, and acidity of mixed SOA and ammonium sulfate particles in controlled laboratory studies (flow tube and chamber) and field measurements. Decreased uptake of IEPOX and conversion of inorganic to organic sulfate lead to important modifications of aerosol physicochemical properties and has large implications for aerosol impacts on air quality and climate.

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Formation and evaporation of organic aerosol from a kinetic modeling perspective

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Formation of Secondary Organic Aerosol (SOA) was investigated at the Georgia Tech Environmental Chamber (GTEC) facility from separate, simultaneous and sequential oxidation of the terpenic precursors α-pinene and limonene with the nitrate radical (NO3). Aerosol formation was initiated at low temperatures of 5 °C and evaporation of product species monitored during step-wise heating of the reaction chamber to 42 °C. α-pinene and limonene SOA showed distinct patterns in formation and evaporation upon increase in chamber temperature.

In this presentation, we will discuss how the results from these experiments can be interpreted using a kinetic model that utilizes a multi-layer aerosol model alongside a global optimization algorithm and machine-learning techniques. The novel approach allows for the extraction of microscopic information from macroscopic data, despite the inherent complexity of a multiphase chemical reaction system such as the formation of SOA. Special attention will be given to gas-phase radical chemistry, temperature-dependent gas-particle partitioning of reaction products and diffusion within the particles.

As will be outlined in the presentation, the model shows evidence for kinetic limitations in the evaporation of organic material and a phase transition during the heating process. Furthermore, the model generated a semi-explicit chemical mechanism that simplifies existing comprehensive mechanisms of atmospheric chemistry, which is a crucial prerequisite for efficient modelling of organic aerosol formation in larger scale models.

Based on these results, the capabilities of kinetic multi-layer models in studying organic aerosol formation will be critically evaluated and potential directions for cooperation between theorists and experimentalists will be discussed.

Multiphase Chemistry Contributions to SOA Formation

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In the first part results from the Leipzig Aerosol Chamber (LEAK) and select field investigations will be presented and discussed dealing with the formation of highly oxidized molecules (HOMs) from terpenes and isoprene and their transfer into the particle phase. Here, investigations of ozone and OH initiation (for the terpenes) and of OH only (for isoprene) will be discussed with emphasis on uptake and particle phase analytics. Molecular mechanisms will be outlined and the potential impact of HOMs transfer on particle oxidant levels will be studies by CAPRAM modelling.

In the second part, a newly developed CAPRAM module to treat HOMs and isoprene oxidation products will be described and results are presented. The compound studied are shown to contribute to the OH-in-particle-budget as well as increase organic particle mass. A summary addressing possible impacts and an outlook will be given.

Computational insights into formation mechanisms and properties of atmospheric autoxidation products

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Peroxyradical (RO_2) - based autoxidation mechanisms have recently been established as a potentially important source of highly oxidized, and thus potentially extremely condensable, monoterpene degradation products. Much of the detailed mechanistic information on atmospheric autoxidation has been obtained from studies of relatively small molecules such as isoprene or cyclohexene. The autoxidation pathways of the chemically more complex monoterpenes may involve additional reactions not present in these systems.

Recent computational studies suggest some general rules of thumb for monoterpene autoxidation. One important finding is that most or all reactions (including for example both H-shifts and alkoxy bond scissions) leading to the formation of alkyl radical centers on C_3 or C_4 rings are likely to be non-competitive in atmospheric conditions. This is likely a major factor in explaining for example the large difference in aerosol yields in NO_3 – initiated oxidation of different monoterpenes.

The precise mechanism for the formation of covalently bound "dimer" products (with twice the number of C atoms compared to the parent monoterpene) remains unresolved. Experimental evidence strongly points toward $RO_2 + RO_2 \Rightarrow ROOR + O_2$ recombination reactions as the source of the observed dimers, while computational studies indicate high barriers for direct recombination. One possible explanation is that the dimer formation reaction involves the formation of two alkoxy radicals, coupled as a triplet, and requiring an intersystem crossing to the singlet surface to form ROOR.

Another area of significant uncertainty concerns the saturation vapor pressures of autoxidation products containing multiple peroxy groups. Traditional group contribution methods lack parameters to describe intramolecular hydrogen bonding between these groups, leading to underestimated saturation vapor pressures. Conversely, the quantum-chemistry based COSMO-RS method (as implemented in the COSMOTherm program) tends to overestimate the effect of intramolecular hydrogen bonding, leading to overestimated vapor pressures. COSMOTherm predictions can be improved by first performing a systematic conformational sampling, and then selecting conformations with a reduced number of intramolecular bonds.

Development of a predictive aerosol viscosity model

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The viscosity of airborne particles is a key factor in determining atmospheric aerosol processing and growth/evaporation. Liquid or semi-solid particle phases of high viscosity affect dynamic gas-particle partitioning of semivolatile organic and inorganic compounds due to very slow diffusion in the condensed phase and may substantially affect water uptake in the case of a glassy physical state[1]. Highly viscous organic particle phases also affect the ability of aerosols to act either as cloud condensation nuclei or ice nuclei under tropospheric conditions[2]. In recent years, several new experimental techniques have been developed to measure bulk phase and aerosol particle viscosity as a function of chemical composition and temperature[2]. These measurements provide new data to explore the relationships of mixture composition and viscosity of aqueous organic systems and their representation by physicochemical models. Existing predictive models of mixture viscosity tend to perform poorly at viscosities exceeding 1 Pa s, which is the case for all mixtures in the semi-solid range and beyond. We introduce a new, semi-empirical predictive method based on the thermodynamic model AIOMFAC and modifications of the approach by Cao et al. (1993)[3]. We show that this model is capable of representing the change of viscosity with mixture composition, most importantly water content, over the extensive range from water-like liquids to the viscosity of glasses. In the case of multicomponent mixtures as surrogates of organic aerosols, an important factor in the accuracy of viscosity predictions is the estimation of pure component viscosity as a function of temperature for complex organic compounds. We will discuss an assessment of different pure component viscosity estimation approaches as well as the use of experimental data from binary aqueous organic solutions, where available, to constrain the range of adequate pure component values with our model.

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Water interactions with an organic nopinone surface: a combined theoretical and experimental study

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The detailed description of organic aerosols in the atmosphere remains a major challenge, which limits our ability to understand and predict environmental change. Important research questions concern the hydrophobic/hydrophilic character of fresh and aged aerosols and the related influence on water uptake. A picture of the detailed molecular-level behavior of water molecules on organic surfaces is beginning to emerge based on detailed experimental and theoretical studies [1]; one example is a recent study that investigates water interactions with solid and liquid *n*-butanol near the melting point [2]. Here we employ Environmental Molecular Beam (EMB) experimental techniques and Molecular Dynamics (MD) simulations to characterize water trapping-desorption processes on a nopinone surface. Nopinone ($C_9H_{14}O$) is a reaction product formed during oxidation of β-pinene and has been found in both the gas and particle phases of atmospheric aerosol. We show that a classical force field for organic material is able to model crystal and bulk structure. The surface properties near the melting point of the condensed phase are reported, and the hydrophobic and hydrophilic character of the surface layer is discussed. Results from MD simulations are compared with EMB results for water interactions with a nopinone surface, and we evaluate the influence and behavior of water-nopinone conformation structures that are accessible in this rather hydrophobic system.

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Micro-spectroscopic characterization of particles generated from mesocosm and collected over South China Sea

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Aerosol particles are often not a single compound residing the atmosphere, but rather a mixture of e.g. soot, organic and inorganic materials. The marine environment is one major source of atmospheric particles due to the direct emission of sea salts and biogenic/organic matter. A wealth of research in the recent years has been investigated the capability of these mixed organic/inorganic particles to act as cloud condensation and ice nuclei with implications for cloud formation and precipitation. During transport of airborne particles in the atmosphere, chemical and physical aging can alter their physicochemical properties. In turn, freshly emitted and aged particles may pose different environmental and climatic impacts. Here we present micro-spectroscopic characterization of particles collected during cruises over the South China Sea or generated by bubble busting during a mesocosm experiment. Two single particle techniques, scanning transmission X-ray microscopy coupled with near-edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) and computer-controlled scanning electron microscopy coupled to energy dispersive X-ray analysis (CCSEM/EDX), were applied to hundreds of individual particles to obtain information on the particle elemental composition and spatially resolved mixing state at statistically significant level. The mixing state is a quantitative measure which is the number of particles having a single component or a combination of the components which are soot, organic and inorganic matter. These results will be discussed on cloud formation ability with a particular focus on the ice nucleation potential of these field and laboratory generated particles.

Experimental and theoretical investigation of HO_2 sticking on dicarboxylic acid aerosols

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Many uncertainties are still associated to chemical reaction mechanisms used in atmospheric models, in particular for RO_x radicals (OH, HO_2, RO_2). Recent measurements of radicals in forested areas characterized by low NO_x (NO_2, NO) concentrations indicate that models can significantly overestimate peroxy radical concentrations.[1,2] These results question the ability of models to correctly simulate the oxidative capacity of the troposphere since peroxy radicals are a main source of the hydroxyl radical (OH), one of the most important oxidative species in the atmosphere.[3] One possible explanation is the occurrence of heterogeneous processes (uptake of radicals) on the surface of aerosols that are either underrated or not included in models. While recent studies have reported uptake coefficients of HO_2 on different types of aerosols, uptakes of RO_2 radicals have yet to be investigated.

The aim of this work is to investigate HO_2 and RO_2 uptakes on organic aerosol surfaces, both theoretically and experimentally. A molecular modelling study has been carried out to study the structure (radial distribution function, binding energy distribution, atom surface distribution, etc.) of Glutaric acid ($C_5H_8O_4$) aerosols and the influence of water on it. A comparison with Valeric acid ($C_5H_{10}O_2$) aerosols has also been performed. The mass accommodation coefficient of HO_2 has then been computed for glutaric acid aerosol. To complement the molecular modelling study, an experimental study is also under progress using an Aerosol Flow Tube setup coupled to a PERCA instrument for HO_2 and RO_2 detections.

This work is supported by the CaPPA project (Chemical and Physical Properties of the Atmosphere), funded by the French National Research Agency (ANR) through the PIA (Programme d'investissement d'avenir) and by the regional council "Hauts-de-France". The authors also thank CPER Climibio and FEDER for their financial support. Calculations were performed using HPC resources from GENCI-TGCC (Grant 2017-A0010806820).

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Small-angle X-ray scattering of self-assembled lyotropic phases in single aerosol particles.

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We have demonstrated[1] that acoustic trapping can be used to levitate and manipulate droplets of soft matter, in particular, lyotropic mesophases formed from self-assembly of different surfactants and lipids, which can be analysed in a contact-less manner by X-ray scattering in a controlled gas-phase environment. On the macroscopic length scale, the dimensions and the orientation of the particle are shaped by the ultrasonic field, while on the microscopic length scale the nanostructure can be controlled by varying the humidity of the atmosphere around the droplet. We found in situ phase transitions of micellar, hexagonal, bicontinuous cubic and lamellar phases. The technique opens up a wide range of new experimental approaches of fundamental importance for environmental, biological and chemical research.

Organic atmospheric aerosols often contain both hydrophilic and hydrophobic components, but the nature of how these compounds are arranged within an aerosol droplet remains unknown. We have shown[2] that fatty acids in proxies for atmospheric aerosols self-assemble into highly ordered three-dimensional nanostructures that may have implications for environmentally important processes. Acoustically trapped droplets of oleic acid/sodium oleate mixtures in sodium chloride solution were analysed by simultaneous synchrotron small-angle X-ray scattering (SAXS) and Raman spectroscopy. We showed that the droplets contained crystal-like lyotropic phases including hexagonal and cubic close-packed arrangements of spherical and cylindrical micelles, and stacks of bilayers, whose structures responded to atmospherically relevant humidity changes and chemical reactions. Further experiments demonstrated that lyotropic-phase formation also occurs in more complex mixtures more closely resembling compositions of atmospheric aerosols. We suggest that lyotropic-phase formation likely occurs in the atmosphere, with potential implications for residence times and other aerosol characteristics.

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Exploring the potential for synchrotron radiation based methods to study organic aerosol-water interactions directly at the molecular level

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Despite advances in both aerosol measurement techniques and model formulation, important gaps remain in our fundamental understanding of especially the organic aerosol fraction. This is evident in studies of e.g. new particle formation, aerosol growth and cloud activation, and atmospheric scale cloud effects, as discrepancies between experimental setups and between models and experimental results[1,2]. Over the past decade, we have explored the potential for emerging experimental methods using high-brilliance synchrotron radiation (SR) to shed light on molecular-level interactions between organic aerosol and atmospheric water. With a variety of specialized end-station setups, including supersonic liquid micro-jet, liquid flow cell, deposited aerosol particles, and free-flying droplets and sub-2 nm molecular clusters, we have probed the molecular-level properties of atmospheric particles and droplet model systems in a variety of conditions and phase states[3,4,5]. Using a range of absorption, emission, and scattering based spectroscopic techniques, we have probed different aspects of structure and chemistry, focusing on the key role of aqueous organic surfaces.

Current efforts focus on enhancing the immediate atmospheric relevance of experimental design, including ambient pressures and single particle in-situ studies. The emergence of fourth generation SR facilities like MAX IV Laboratory in Sweden brings great promise in this respect. We are part of the Finnish-Estonian consortium commissioning the Beamline for Atmospheric and Materials Science (FinEstBeAMS). With a wide photon energy range, high brilliance and resolving power, and three complementary end-stations, the beamline enables studies of diverse systems, conditions and properties[6]. We are furthermore taking part in developing mobile instrumentation to specifically enable atmospherically directed research at several beamlines at MAX IV.

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Perspective of X-ray excited electron spectroscopy to probe chemistry and structure at the surface of aerosol proxies

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X-ray excited electron spectroscopy encompasses X-ray photoelectron spectroscopy (XPS) of typically core atomic electronic levels and electron yield near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The low inelastic mean free path of electrons of a few nanometer enables sensitivity for the condensed matter – gas interfacial region. Recent advances in the development of differentially pumped electrostatic lens systems have allowed experiments with both high vapor pressure materials (solid or liquid) or materials exposed to high reactant pressures in the mbar range. This has offered tremendous opportunities for molecular understanding of atmospherically relevant aqueous solution surfaces [1,2], ice surfaces [3,4], and mineral oxides [5], all in presence or absence of reactive trace gases and in or out of equilibrium with water vapor. Examples related to the protonation state of acids at the aqueous solution – vapor interface and to the structure of water at mineral oxide interfaces will be given. The high vapor pressure in the sample region comes along with losses of electrons by scattering in the gas phase, which becomes a problem with suspended aerosol particles. Aerodynamic focusing of particles to achieve higher local particle density and thus also photo-electron current densities comes along with pressures not allowing aerosol particles remaining in equilibrium with water vapor, and other detector types with larger electron acceptance angles have not yet become operational for enhanced pressures. In turn, this still allows substantial opportunities for the fundamental understanding of small particles, e.g., effloresced salt particles or mineral particles under conditions where the presence of high bath gas pressures is not so relevant.

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Uptake of atmospheric molecules on acid clusters

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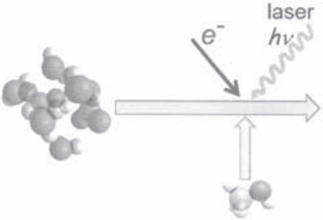
Mixed acid clusters $(HNO_3)_M(H_2O)_N$ and $(H_2SO_4)_M(H_2O)_N$ can represent model systems to mimic aerosol particles in laboratory molecular beam experiments [1]. We investigate the pickup of various atmospheric molecules, e.g. isoprene, α-pinene, hydrogen halides etc., by these acid clusters. A combination of the cluster mass spectrometry with velocity measurements has enabled us to determine the absolute pickup cross section for methanol molecules on nitric acid clusters [2]. We can compare the uptake of other molecules to methanol determining the relative pickup probabilities. By the way of example, the oxidized derivatives of isoprene 2-methyl-3-buten-2-ol and 3-methyl-3-buten-1-ol pickup with about 50% probability compared to methanol on the acid clusters, while isoprene is picked up with only 2% probability compared to methanol. Similar probability ratio for pickup is also measured between verbenol, the oxidized derivative of α-pinene, and α-pinene. The molecules seem to anchor efectively to the clusters via the OH groups generating hydrogen bonds.

We have also investigated the attachment of slow (1-10 eV) electrons to these acid clusters. The electron (and eventually photon) triggered chemistry [3,4] in these particles will be also discussed if time permits.



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Abstracts of Posters

(in alphabetical order)

Application of Nonlinear Optical Spectroscopy in Molecular Level Characterization of Atmospheric Aerosol-Water Interactions

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Over decades, the observations of atmospheric processes bridged the scales from macroscopic to microscopic levels. They delivered a wide variety of results, particularly concerning the ice nucleation ability of atmospheric aerosol particles, and hence the mechanisms of cloud dynamics, precipitation formation and interaction with incoming and outgoing radiation. For example, the structural and chemical properties of the surface of an ice nucleating particle (INP) play a major **but not** well explored role in its interaction with water molecules in atmosphere. There is still a fundamental shortcoming in our knowledge about 1) the role and weight of different chemical or physical surface properties and 2) the molecular structuring of water at the aerosol surface under different atmospheric conditions.

To improve our understanding of atmospheric aerosol-water interactions, a molecular level probe has become a demand. Nonlinear optical spectroscopy, mainly second-harmonic and sum-frequency generation (SHG, SFG) are powerful, interface selective and monolayer sensitive techniques capable of exploring surface interactions on the molecular level. Such studies have recently become possible at the KIT after two successful DFG grants (AB 604/1-1 and AB 604/1-2) [1-3]. The talk will present a novel approach using supercooled SHG and SFG experiments to investigate aerosol-water interactions. An overview of recent findings including the effect of surface-charge and adsorbed ions on water freezing on mineral INPs and future plans on biological INPs will be presented.

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Iron Oxidation as a Tracer for Radical Reactions Inside Organic Aerosol Particles.

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Airborne organic matter can be in a highly viscous or glassy phase with properties comparable to that of a solid. Diffusion and reaction of oxidizing trace gas molecules in highly viscous organic aerosol can be limited and lead to an inhomogeneous reactant and product concentrations. Due to the abundance of oxygen in the atmosphere, one could assume oxygen molecules saturate small (<1 µm in diameter) aerosol particles throughout their bulk. We challenge this standpoint and hypothesis that condense phase radicals formed uniformly from photochemical reaction in viscous organic aerosol can effectively limit oxygen reaction only at particle surfaces, and thus aerosol particle interiors remain anoxic. Photochemically produced radicals are likely to exhibit as slow of a diffusion as host organic matter and thus, may be preserved or remain environmentally persistent. We present a study using scanning transmission X-ray microscopy coupled to near edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) to visualize the photochemical reaction of Fe-citrate complex and reoxidation in the presence of O_2. We find that photochemical reaction of Fe(III)-citrate particles leaves their interiors entirely reduced and remains so for hours after irradiation stops. This is evident through our direct observation of Fe oxidation state with a spatial resolution of 35x35 nm. Using a multi-layer molecular reaction and diffusion model, we predict the formation and persistence of Fe oxidation state. We conclude that the concentration of free radicals (FR) and reactive oxygen species (ROS) can explain recent ambient measurements of environmentally persistent free radicals. This implies that photochemical processing of aerosol particles may extend the lifetime and increase the concentration of FR and ROS species (which are well known to cause oxidative stress in human lung tissue) more than previously suspected when considering organic viscosity and molecular diffusion.

Towards using the photophoresis for measurements of light absorption by a single particle

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The surface of an illuminated, light absorbing particle is, most likely, unevenly heated relative to its surrounding. The temperature difference between the illuminated and the 'dark' side of the particle results in an uneven momentum transfer from colliding gas phase molecules.[1] This leads to a net photophoretic force (F_{ph}) acting on the particle in the direction of the momentum transfer gradient. The heat distribution within the particle is related to its complex refractive index (RI) and to its size parameter through the irradiant internal fields. As such, it may lead to a higher temperature either at the illuminated or at the non-illuminated side and to a net force away from (positive) or towards (negative) the light source correspondingly.[2] Here, we report on preliminary attempts to use this phenomenon to quantify accurately light absorption by a single, slightly absorbing particle levitated in an electrodynamic balance (EDB). Our goal is to improve sensitivity and precision relative to current methods used for quantification of light absorption by laboratory generated and ambient aerosols.[3] In the EDB setup, the power that is required to levitate a particle is directly proportional to the vertical net force acting on the particle. With current signal to noise ratio, it is possible to quantify a change as low as 0.1% in the net vertical force. For a micron-sized particle and visible range light source, this corresponds to an imaginary part of the complex RI in the range of 10^{-5} to 10^{-3}. An additional advantage of the EDB is that heterogeneous chemistry and photochemistry experiments, on a single particle, are performed with realistic atmospheric gas concentration and aging time. In such experiments, continues or occasional probing of the particle's light absorption properties using the F_{ph} would add valuable information on the evolution of light absorption by ageing or secondary organic aerosols.

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Hypercooled Water

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For deeply supercooled liquids the transition from a two-stage freezing process to complete solidification in just one freezing step occurs at the hypercooling temperature, a term that seems to be almost unknown in water research; to our knowledge, it has only been mentioned by Dolan et al. for high-pressure ice. The reason for the absence of this expression may be that the best estimate to be found in the literature for the hypercooling temperature of water is about −160 °C (113 K). This temperature is far below the limit of experimentally realizable degrees of supercooling near −40 °C (233 K), which marks the homogeneous nucleation temperature TH of common pure water; in fact, it is even below the glass-transition temperature (133 K). Here we show that, surprisingly, a more thorough analysis taking into account the temperature dependence of the heat capacities of water and ice as well as of the enthalpy of freezing shows that the hypercooling temperature of water is about −64 °C or 209 K, almost 100 K higher than estimated before. One of the most exciting consequences is that existing experiments are already able to reach these degrees of supercooling, and it is our prediction that a transition in the freezing behavior occurs at these temperatures.

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Measurements and Modelling of Surfactant Coated Aerosol Particles

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The surface tension of atmospheric particles is key to determining the critical supersaturation required for a particle to activate into a cloud condensation nucleus. Most models generally assume the surface tension of activating particles is equivalent to that of pure water. However, recent experiments and field measurements have shown that the surface tension of particles can be much less than that of pure water, for instance due to the presence of condensed organic films, core-shell phase separations, and/or surfactants. For surfactants to be relevant to particle activation into cloud droplets, at least two parameters must be considered. First, the concentration of surfactant in the initial particle must be sufficiently large that surface tension depression is maintained over the course of activation, despite the dilution that occurs as water condenses onto the particle. Second, the high surface to volume ratio of micron and submicron particles necessitates partitioning of more surfactant molecules to the particle surface than in a typical solution, resulting in a depletion of the bulk concentration and an increase in the surface tension relative to a bulk sample.

This presentation will provide a comprehensive account of the size dependent partitioning behaviour of surfactant containing particles through a combination of measurements and modelling. The experimental approach utilises holographic optical tweezers, which allows quantification of the surface tension of picolitre volume surfactant-containing droplets by monitoring of the periodic shape oscillations resulting from controlled coalescence of two droplets.[1] These experiments show that surface-bulk partitioning can result in a difference of >10 mN/m between the droplet measurement and the bulk measurement at the same nominal concentration. Experimental data compare favourably to a surface monolayer model constrained only by bulk measurements.[2] As a result, particle surface tension can be modelled to determine the sensitivity of particle surface tension to particle size and surface tension. This approach therefore will provide key information about the significance of the surface tension assumptions inherent in climate models.

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Chemical Transformation of Organosulfates through Heterogeneous OH Oxidation: Formation of Inorganic Sulfate and Sulfate Radical Anion Chemistry

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Organosulfates are important organosulfur compounds present in atmospheric particles. While the abundance, composition, and formation mechanisms of organosulfates have been investigated, it remains unclear how they transform throughout their atmospheric lifetimes. To acquire a fundamental understanding of how organosulfates chemically evolve, this work investigates the heterogeneous OH radical-initiated oxidation of sodium methyl sulfate (CH_3SO_4Na), the smallest organosulfate detected in atmospheric aerosols, using an aerosol flow tube reactor at a high relative humidity of 85 %. Aerosol mass spectra measured by a soft atmospheric pressure ionization source (Direct Analysis in Real Time, DART) coupled with a high-resolution mass spectrometer showed that neither functionalization nor fragmentation products are detected. Instead, the ion signal intensity of the bisulfate ion (HSO_4^-) has been found to increase significantly after OH oxidation. We postulate that sodium methyl sulfate tends to fragment into a formaldehyde (CH_2O) and a sulfate radical anion ($SO_4^{\bullet-}$) upon OH oxidation. The formaldehyde is likely partitioned back to the gas phase due to its high volatility. The sulfate radical anion, similar to OH radical, can abstract a hydrogen atom from neighboring sodium methyl sulfate to form the bisulfate ion, contributing to the secondary chemistry. Kinetic measurements show that the heterogeneous OH reaction rate constant, k, is $(3.79 \pm 0.19) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} with an effective OH uptake coefficient, γ_{eff}, of 0.17 ± 0.03. While about 40 % of sodium methyl sulfate is being oxidized at the maximum OH exposure (1.27×10^{12} molecule cm^{-3} s), only a 3 % decrease in particle diameter is observed. This can be attributed to a small fraction of particle mass lost via the formation and volatilization of formaldehyde. In general, the heterogeneous OH oxidation of an organosulfate can lead to the formation of sulfate radical anion and produce inorganic sulfate. Fragmentation processes and sulfate radical anion chemistry play a role in determining the compositional evolution of sodium methyl sulfate during heterogeneous OH oxidation.

Aerosol Optical Properties during Homogenous and Heterogeneous Brown Carbon Formation

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The light absorption by brown carbon (BrC) aerosol is highly uncertain, with BrC composed of a diverse range of organic chemical species that absorb light strongly at optical wavelengths < 500 nm. Recent studies show that BrC aerosol radiative forcing estimates vary by a factor of ~ 10 over a range of +0.04 to +0.57 W m^{-2} [1,2]. 40% of black carbon aerosol and 70% of organic carbon particles originate from biomass burning [3]. Field measurements of biomass burning aerosol observe that the BrC contribution to light absorption evolves with particle age; the absorption Angstrom exponent (AAE) increases during ~ 1 hour after emission and then decreases significantly over timescales of days [4]. Understanding the chemical aging of BrC and impact on aerosol optical properties is crucial for improved representation of aerosol-radiation interactions in climate models. BrC formed through reaction of glyoxal (GO) or methylglyoxal (MGO) with ammonium sulfate (AS) has seen interest in recent years [5,6], with GO and - to a limited extent - MGO estimated to contribute significantly to aqueous organic aerosol composition [7].

This work uses cavity ring-down and photoacoustic spectroscopy to measure aerosol extinction and absorption ensemble cross sections at 405, 515 and 660 nm laser wavelengths. We report measurements of these optical cross sections and retrieved refractive indices for BrC aerosol formed from the reaction of AS with either GO or MGO. We present data for homogeneous reactions of AS with MGO inside aqueous droplets, demonstrating enhanced reaction rates in aerosol compared to in bulk solution. We also consider heterogeneous reactions of AS seed particles with gaseous GO. Our results represent the first direct *in situ* measurements of light *absorption* by aerosol for the aforementioned BrC formation reactions; previous studies either assessed absorption in bulk solutions or inferred absorption from separate aerosol extinction and scattering measurements [8] that are subject to high uncertainties in the limit of weak absorption.

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Digital holography of optically-trapped aerosol particles

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Many processes associated with aerosol particles remain poorly understood. These processes include phase transitions, photochemistry, interfacial chemistry, interaction with light, optical binding and coupling of translational and rotational motion of nonspherical particles.The morphology (size and shape) of aerosol particles is a key parameter in these processes. However, the particle morphology and its time evolution is also one of the most difficult properties to investigate. Usual optical microscopy techniques suffer from some important limitations to image the morphology of aerosol particles. Their fixed imaging plane causes blurred imaging upon fast motion of the particle. In addition, they do not provide information on the particle's 3D position, orientation and morphology.

In this contribution, we will present the combination of a new digital holographic microscope with counter-propagating optical tweezers (CPT). The CPT confines and isolates particles in air over extended periods of time (up to several days when necessary) to study the process of interest. Meanwhile, holographic imaging measures the 3D morphology, trajectory, and orientation of the optically trapped aerosol particles with high temporal and spatial resolution (240 µs and 770 nm, respectively) [1]. The first results obtained with this experiment will be discussed, including the monitoring of the rotation and translation of trapped non-spherical particles, the measurement of the time evolution of the optical forces acting on a particle, and the observation of the complex trajectory of two optically-bounded particles. We currently also exploit this experiment to improve our understanding of the multistep efflorescence and deliquescence observed for aerosol particles [2].

This work was supported by the Swiss National Science Foundation (SNSF grant no. 200020_172472), ETH Zurich and an ETH Career Seed Grant SEED-67 16-1.

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Single Droplet Photoacoustic Spectroscopy

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Photoacoustic (PA) spectroscopy is a well-established tool for measuring absorptive properties of aerosols due to its high sensitivity and ability to study unsupported aerosols. When combined with an optical trap, the Single Particle Photoacoustic Spectrometer (SP-PAS) [1] enables size-resolved absorption measurements of submicron-range particles. In such an experiment, two counter-propagating Gaussian beams are tightly focused onto an aerosol particle, trapping it in the surrounding gas, while the modulated PA IR laser is shone onto the particle creating acoustic waves which are detected by a microphone (Figure 1).

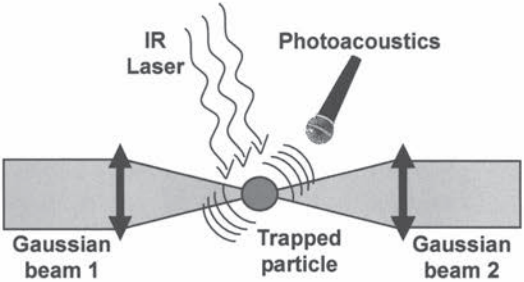

Figure 1. Photoacoustic spectroscopy of a single optically-trapped aerosol particle

However, PA spectroscopy is not without its own set of challenges – namely the biases at large particles' radii and at elevated relative humidities. SP-PAS opens an experimental window towards a fundamental understanding of the physical processes behind the PA signal generation and hence offers an experimental benchmark for the aforementioned biases predicted by theory. [2,3]

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Iron Reoxidation in Photochemical Cycling

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Iron (Fe(III)) carboxylate complexes in aerosol particles absorb light below about 500 nm followed by ligand to metal charge transfer (LMCT) which reduces Fe(III) to Fe(II) and oxidizes carboxylate ligands[1]. When O_2 is present, production of radicals, peroxides and oxygenated volatile organic compounds (OVOC) ensues. Importantly, radicals (e.g., OH•, HO_2• and RO_2•) reoxidize Fe(II) to Fe(III) and can then complex with neighboring acid groups closing a photocatalytic cycle.

We investigated iron carboxylate catalyzed photochemistry by tracking mass and size changes of single, levitated organic aerosol particles in an electrodynamic balance (EDB) under visible (473 nm) light irradiation as a function of relative humidity (RH). Particle had an around 10 μm radius and contained Fe(III)-citrate in aqueous citric acid with a mole ratio of 0.05. A mass loss was observed during Fe(III)-citrate photochemistry due to the evaporation of volatile (e.g., CO_2) and semi-volatile (e.g., ketones) products. To quantify Fe(II) to Fe(III) reoxidation we first exposed the particle to N_2 and light until all Fe(III) reduced to Fe(II), and then switched off light and introduced O_2. At 48% RH, we found that 10 hours exposure to O_2 was sufficient for all Fe(II) to be reoxidized while at 24% RH, complete reoxidation after 25 hours was not yet achieved. We attribute the differences in recovery time to the O_2 diffusion limitations (i.e., limited O_2 availability for reoxidation) at lower RH. To better understand the interplay of photochemical reaction pathways and molecular diffusion in our system, we developed a numerical model to simulate Fe(III)-citrate photochemical cycling in single particles. Molecular diffusion coefficients of CO_2 and O_2 as a function of RH, and the oxidation rate of Fe(II) by O_2 directly were derived using our model. With these well-defined and physically constrained parameters, we predict the evolution of products as well as organic acids degradation in the condensed phase under atmospheric conditions.

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Towards Modelling the Catalytic Effect of Atmospheric Molecular Clusters

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Atmospheric chemistry is traditionally partitioned into either gas-phase chemistry or heterogenous chemistry that takes place within the bulk or the particle phase. We report the first steps towards elucidating the atmospheric chemistry that exists in between these two extremes – the chemistry at the interface of atmospheric molecular clusters. Measurements in the ambient atmosphere have identified that there exists a continuous background mode of clusters with number concentration ranging up to 100.000 clusters/cm^3. The chemical composition of these clusters remain uncertain, but both computational and experimental evidence suggests that the most stable clusters consist of sulfuric acid and bases. Small particles have been shown to be being unexpectedly acidic, which has important implications on atmospheric chemistry, as organic and inorganic acids can act as gas-phase catalysts, that highly reduce the reaction free energy barrier via double hydrogen atom transfer reaction routes.

Using state-of-the-art quantum chemical methods the hydrolysis of formaldehyde (H_2CO), forming the corresponding diol, is studied at the interface of clusters consisting of 3 sulfuric acid and 3 ammonia, with varying water content: $(H_2SO_4)_3(NH_3)_3(H_2O)_{1-3}$. Figure 1 presents an example of one of the identified transition states where sulfuric acid in the cluster act as a catalyst in the hydration reaction.

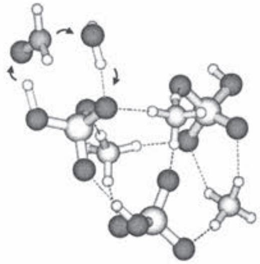

Figure 1 - The identified transition state structure for the hydrolysis reaction of formaldehyde occurring at the interface of a $(H_2SO_4)_3(NH_3)_3(H_2O)_1$ cluster. The arrows indicate the atomic motion in the transition state. Brown = carbon, red = oxygen, blue = nitrogen, yellow = sulfur and gray = hydrogen.

It is found that the cluster can catalyse the formaldehyde hydration reaction, but it is unlikely that the studied reaction will take place under ambient conditions. The potential implications of cluster catalysis in the ambient atmosphere, in smog chamber experiments and future prospects for multiscale modelling of aerosol surface reactions is presented.

Single particle spectroscopy: 1064 nm Raman and the use of probe molecules

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Observation of particles in the true aerosol phase provides an accurate picture of their chemical and physical characteristics. Here we present spectroscopic measurements from single particles levitated using near-IR laser tweezers which are capable of stably trapping a variety of particle types (solid, liquid) for hours-days.

We deploy two spectroscopic techniques: Raman spectroscopy and Fluorescence Lifetime Imaging (FLIM). Raman spectra provide rich information about particle chemical composition. However, for particles containing organic compounds, the use of visible or UV lasers for Raman excitation can result photo-degradation or overwhelming fluorescence. Here we present our unique ability to use the same near-IR laser (1064 nm) for particle levitation and interrogation [1]. This allows us to continuously acquire fluorescence-free spectra over long experiment times.

We will also discuss work using molecular probes to report on local chemical environments in the aerosol, *via* changes in fluorescence lifetime. Our previous work using fluorescent molecular rotors to report on particle viscosity [2] will be extended to include discrete particle phase transitions. Furthermore, we will present initial work using green fluorescent protein (GFP) as a probe of particle refractive index [3]. Finally, we will provide perspective on the wider use of molecular probes for a range of aerosol properties.

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A High Resolution Cryogenic Single Nanoparticle Mass Spectrometer

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Diverse nanoparticles, originating from natural or anthropogenic sources, exist in the atmosphere where they directly, through scattering and absorbing of sunlight, and indirectly, by serving as cloud condensation nuclei (CCN), affect the climate. Especially their ability to act as CCN is an important but not well understood aspect of cloud model simulations. Since clouds cover roughly two thirds of the globe they play a striking role in simulations of world's climate but their formation mechanism still remains one of the greatest uncertainties. To improve the quality of such simulations the nanoparticle properties, e.g. surface structure and reactive behaviour, have to be characterised experimentally.[1,2]

Motivated by the work of the groups of Gerlich and Anderson[3-5] we developed a cryogenic, single nanoparticle mass spectrometer to investigate the surface structure and reactive behaviour of a broad range of nanoparticles in the size range of 5 to 50 nm. A single nanoparticle from a nanospray ion source is trapped in a custom-designed quadrupole ion trap which is mounted on the second cooling stage of a closed-cycle Helium cryostat. The particles mass-to-charge ratio m/z is accurately measured by optically monitoring the particles secular oscillation frequency. This enables us to monitor m/z variations of a single nanoparticle, depending on temperature (10-350 K), background gas and interaction with light over several days.

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Computational prediction of the chemical signatures of autoxidation of organic aerosol under atmospheric conditions

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Autoxidation has been invoked as an important mechanism for formation of highly oxidized organic species in the atmosphere via gas phase unimolecular pathways [1], however little is known about whether it is also important in heterogeneous oxidation, particularly under tropospheric conditions. In order to explore this question, we have carried out a computational study of the effect of autoxidation on reactivity as a function of particle viscosity. The reaction-diffusion scheme we have used has been developed and validated for the heterogeneous oxidation of model $C_{30}H_{62}$ alkane aerosol, ranging from liquid and semi-solid, by OH radicals [2]. OH concentrations of $2x10^4$ cc^{-1} (night conditions), 10^6 cc^{-1} (day conditions), and diurnal cycling for a reaction time of one week, which is typical of aerosol lifetimes, were used. The scheme provides detailed information on chemical composition of the aerosol and its surrounding gas as well as particle size as a function of time and particle viscosity. In this study, two sets of calculations have been performed, one without autoxidation, and one with autoxidation steps added to the base mechanism. The results show that while the chemical signs of particle phase autoxidation are subtle under all conditions when the particle is well-mixed, autoxidation becomes important as particles become more viscous. Autoxidation accelerates oxidized product formation, focusing products in the particles nearly exclusively toward ketones and peroxy radicals, and is dramatically enhanced at night even though the OH density is much lower. This is due to OH production in/on the particle, and longer free radical chains. Diurnal cycling is dominated by daytime chemistry, with overall greater oxidation when autoxidation reactions are included. Little particle volatilization takes place at night, but it can be significant during the day, leading to marked volume loss. These predictions can be tested experimentally. A comparison of measurements to the calculations will provide new insights to aerosol autoxidation processes.

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Heterogeneous freezing on thin sections of K-feldspar: active sites vs. surface chemistry

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Ice formation on aerosol particles is a process of crucial importance to Earth's climate and the environmental sciences, but it is not universally understood at the molecular level. Recently, using environmental scanning electron microscopy we have identified the unique features on potassium-feldspar responsible for its high ice nucleation efficiency. We have hypothesized that these surface features should be universally active in any heterogeneous freezing mode. In this contribution, we present experimental evidence that this is indeed the case for the immersion nucleation of ice on the surface of potassium feldspar (microcline). We compare the freezing behavior of feldspar powder suspensions vs. pure water droplets deposited onto the thin sections of feldspar prepared at different crystallographic orientation. This method allows us to evaluate the surface number density of ice nucleation active sites as a function of crystallographic orientation of feldspar face. In a series of experiments conducted with feldspar immersed in solutions of ammonium salts, we confirm the recent observation of an enhanced ice nucleation efficacy due to the presence of ammonium ion. Interestingly, the shift of characteristic freezing temperature is similar for all crystal planes and powder samples used in our experiments.

Additionally, we address the question of a strong variability of ice nucleation efficiency of K-feldspars by using the IR spectroscopy sensitive to the surface hydroxyl groups. Using a combination of analytical methods, we have compared two specimens of potassium feldspar different in their chemical and structural heterogeneity. Here, we report a strong correlation between the stability of hydroxyl groups on the mineral surface and its ice nucleating efficiency.

SERS pH nanoprobes in single, levitated aerosols particles

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Surface enhanced Raman scattering (SERS) pH nanoprobes are used for assessing pH in micron size, single aerosol particles levitated in an electrodynamic balance. The so-called nanoprobes consist of multiple gold nanoparticles with the pH sensing capacity realized via surface functionalization of the particle with the pH sensitive molecule 4-mercaptobenzoic acid (4-MBA) [1].

Figure 1 shows spectra of a levitated aqueous polyethylene glycol droplet at two different relative humditities (RH), under dry conditions and at about 95% RH.

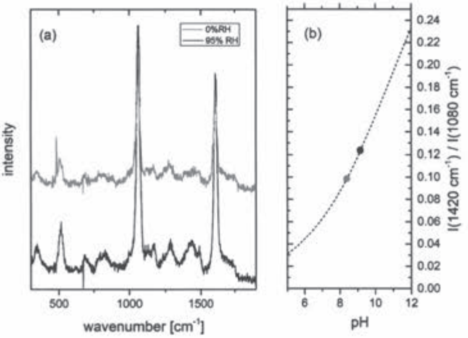

Figure 1: (a) SERS spectra taken of an aqueous polyethylene glycol particle containing nanoparticles at 15 °C under dry conditions (red line) and under humid conditions (95% RH, black line). (b) pH calibration curve (dotted line [1]), solid points are the ratios calculated from (a).

The most prominent Raman band observed in these spectra is that of the benzene ring of 4-MBA at 1080 cm-1). This band remains constant upon changes in solution pH while the band at 1420 cm-1 (-COO$^-$) decreases in intensity and shifts slightly in position with decreasing pH. Measurements in buffer solution have been used to construct the pH-calibration curve shown in panel (b) [1]. According to this calibration, the pH of the levitated, aqueous solution droplet decreased from 9.16 under humid conditions to 8.39 under dry conditions. Buffered aqueous solution droplets are investigated to establish the stability of the calibration curve in the high ionic strength regime, as aerosol particles will become supersaturated with respect to crystalline phase upon drying.

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The volatility of ice below 160K

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Amorphous solid water (ASW) is probably the most abundant form of water in the universe. It forms when water vapor deposits at low temperatures. At temperatures above about 130K ASW crystallizes on time scales below one day, thereby forming nano-crystalline ice. Up to now, the saturation vapor pressure of ASW and nano-crystalline ice were not well characterized, but are crucial to describe the sublimation and growth of interstellar ices or cold ice cloud formation in planetary atmospheres, e.g. polar mesospheric clouds on Earth and H_2O clouds on Mars.

In this contribution, we present results from a laboratory experiment which is designed to study ice nucleation and growth processes on nanoparticles at temperatures below 150K. We use the ice growth-rate on nanoparticles at low and high supersaturation to evaluate for the saturation vapor pressure of ice phases deposited below 160K. We conclude, that ASW initially deposits, followed by temperature activated crystallization to nano-crystalline ice with crystal sizes between 7 and 19nm. We show that the saturation vapor pressure of ASW is substantially higher than previously assumed. Previous parameterizations for the saturation vapor pressure of ASW were in part based on differential scanning calorimetry measurements of the heat released during the crystallization process of ASW. We reconcile these measurements with our results by acknowledging the fact that the saturation vapor pressure of nano-crystalline ice is 200 to 300% higher than for macro-crystalline ice. Finally, we present new parameterizations for the saturation vapor pressure of ASW and nano-crystalline ice.

Heterogeneous ice cloud formation at extreme conditions

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Heterogeneous ice cloud formation at extreme cold temperatures below 150K can be encountered in planetary atmospheres, e.g. polar mesospheric clouds on Earth or water ice clouds on Mars. In the case of polar mesospheric clouds on Earth, ice nucleation is activated on sub 2nm meteoric smoke particles. The formation process of ice clouds at such cold temperatures on nanometer sized nuclei is not well understood because no ice nucleation experiments for such conditions existed so far. In this contribution, we present results from a laboratory experiment which is designed to study ice nucleation processes below 150K on nanoparticles on a microphysical scale.

We determine the binding energy/desorption energy of water molecules on the particle material, which allows us to parameterize the amount of water molecules which are adsorbed on a surface as function of temperature and saturation. In addition, we are able to evaluate for the temperature dependent sublimation flux of water molecules from the phase growing on the particles and conclude that the deposited ice polymorph below 150K is amorphous solid water (ASW). We show that the saturation vapor pressure of ASW is higher than previously assumed which significantly affects the ice growth behavior of the particles. We present a new parameterization for the saturation vapor pressure of ASW. Finally, we determine critical saturations for the onset of ice growth and present a method to predict critical saturations needed for cloud formation below 150K. Moreover, we will discuss the influence of the particle charge on the ice formation process.

Modeling Photo-oxidation and Aerosol Uptake of Reduced Sulfur and Nitrogen Compounds

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The generation of secondary organic aerosols (SOAs) often relies heavily on the creation of a sulfate-enhanced core. In agricultural areas, substantial amounts of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) occur concomitantly with reduced nitrogen compounds, primarily ammonia, but also a variety of simple amines [1]. The photo-oxidation of these compounds to form SO_2, which is further oxidized to create sulfate-rich aerosol particles, has been studied in aerosol chamber experiments by collaborators at UC Riverside. Large amounts of SO_2 (and associated aerosol) are generated by photo-oxidation of DMDS, but somewhat less by DMS. By making modest adjustments to previously published kinetic schemes [2], we show that this is expected: DMDS has more direct paths to generate SO_2 than DMS. While methanesulfonic acid (MSA) has been shown to substantially increase the amounts of SOA generated in chamber experiments [3], these kinetic models suggest that MSA generation is not a major product of direct photo-oxidation of DMS or DMDS on their own. In the presence of reduced nitrogen, far more aerosol is generated than expected. Our preliminary modeling results of the photo-oxidation of trimethylamine suggest that oxidation of amines is not rapid enough to substantially change the amount of NO_x in the system in a way that should lead to more SO_2, suggesting that S-N compounds might be heavily involved in the process instead.

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The reaction between sodium carboxylate and ammonium sulfate in internally mixed aerosols

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Ammonia (NH_3) is the dominant volatile base in the atmosphere and plays a key role in the formation of second aerosols, which account for a large fraction of the total fine particles in China[1]. Increases in ammonia emissions are responsible for soil acidification, water eutrophication, serious health effects[2]. Although the partition of ammonia to ammonium by heterogeneous uptake on bulk acids is known well, the report on reverse ammonia reemission from ammonium in particulate matter is still scare. Here, the release of ammonia from internally mixed aerosols including sodium carboxylate and ammonium sulfate is investigated by FTIR-ATR technology. Water-content loss and solid sodium sulfate are observed after a dehydration-hydration cycle, which depend on the carboxylate to ammonium ratios. Moreover, the absorbances of carboxylate and ammonium bands decrease and carboxylic acid peaks increases. The carboxylate to ammonium ratios decide efflorescence RHs and ratios of formed sodium sulfate. Combining all IR spectral changes shows ammonia release attributed to chemical reaction.

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Photochemistry of single trapped organic aerosol droplets in the submicron size range

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The photochemical behaviour of single organic aerosol droplets is studied by optically trapping them with a counter propagating tweezer[1] (CPT) in a controllable environment. Monitoring the elastically scattered light simultaneously by two dimensional angular optical scattering[2] (TAOS) of the CPT laser and by ultraviolet broadband light scattering spectroscopy[3] [4] (BLS), size and refractive index of submicron spherical particles can be determined reliably. Simultaneous information about photochemical reactions is obtained in-situ from the inelastically scattered light of the CPT laser which yields time dependent Raman spectra [5].

By controlling the environment of the organic aerosol droplet, the photochemistry of single organic aerosol droplets can be studied under well-defined reaction conditions[1]. This is achieved by varying the composition of the gaseous fluid surrounding the aerosol droplet, while photochemical reaction can be initiated by various light sources including the CPT laser in the visible and the BLS source in the UV spectral range.

With this approach we are able to follow the temporal evolution of reaction products to study photochemical kinetics of aerosol droplets. Furthermore, we could determine the size dependency of chemical reactions in organic droplets in the submicron range by correlating the temporal evolution of the Raman spectra, which reflect the change in composition, with the simultaneously monitored change in droplet size caused by product formation and evaporation.

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Water interactions with organic surfaces: uptake, accommodation, and ice nucleation

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Organic surfactants play a large role in the atmosphere due to their ubiquity and diversity. Such surfactants have been shown to enhance and/or suppress the adsorption and desorption kinetics of atmospheric particles [e.g., 1,2], and thus can promote and/or hinder water uptake, potentially changing the hydrophilicity of atmospheric nanoparticles. Even molecules dominated by hydrophobic functional groups can exhibit surprising hydrophilic behaviors [3]. As a result of these fundamental molecular processes, alcohol surfactant layers have size and temperature dependent effects on ice nucleation [4] and growth morphology, in addition to molecular water uptake. Herein the results of successive generations of Environmental Molecular Beam experiments that provide molecular-level information on water interactions with organic surfaces are summarized. Water collisions with organic surfaces and the resulting fate of water molecules are examined to illuminate fundamental processes of accommodation and bulk liquid/ice nucleation. The potential effects on cloud evolution and lifetime and thereby impacts on fundamental environmental processes like the water cycle and radiative balance are discussed.

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Water Interactions with Organic Surfaces Insights from Environmental Molecular Beam and Molecular Dynamics studies

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Interactions between water and organic surfaces are of central importance in many system processes on Earth including aerosol particle formation and growth. Much progress needs to be done in the understanding of these processes on a molecular level.

In this study, we present results from the Environmental Molecular Beam (EMB) method (Johansson et al., 2017), which is a technique that enables molecular level studies of interactions between gases and volatile surfaces at near ambient pressure. The EMB technique gives information about molecular collision dynamics, gas accommodation coefficients, residence time, and fraction of thermally desorbed or scattered molecules directed onto the surface. The setup is applied to investigate water interactions with solid and liquid butanol layers, used as a proxy of organic surfaces.

In addition, Molecular Dynamics (MD) simulations, have been performed to mimic the system under conditions close to the experiments, giving some theoretical insight on surface melting, adsorption, absorption and desorption processes. The calculated angular distributions of the desorbed molecules and the retained fraction of kinetic energy show a good agreement with the experimental data. The kinetics of surface and bulk accommodation are discussed including the effects of temperature and changes in the surface structure of the organic film.

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Towards the surface science of ice nucleation on aqueous organic solutions and solid substrates

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The nucleation of ice is an important process in chemistry, physics and atmospheric science. Although ice nucleation has been studied since long, our understanding of ice nucleation is still far from complete, particularly from a molecular point of view. The hydrogen bonding structure of H_2O can be significantly different between liquid water to ice. This structure is responsible for most of the difference in physical and chemical properties between the different aggregation states of water. The difference between the hydrogen bonding structure of liquid water and ice can be experimentally observed by near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge, because it involves resonant transitions into unoccupied molecular orbitals, which are very sensitive to the nearest neighbors of oxygen atoms. NEXAFS spectroscopy can be performed in electron yield mode, in which Auger electrons emitted upon initial core hole excitation are detected, which provides a surface sensitive NEXAFS spectrum. Experiments reported in this work were performed at the near ambient photoelectron spectroscopy endstation (NAPP) at the SIM and NANOXAS beamline at the Swiss Light Source (PSI, SLS).

Since it has been suggested that some organic compounds have the potential to modify the structure of water that influences the nucleation of ice, we have measured electron yield NEXAFS spectra from a liquid jet of aqueous solution containing tetrabutylammonium bromide (TBAB). The O K-edge spectra exhibit a clear change in the relative features. These features represent hydrogen bonding at different level, indicating that the cationic head group of TBAB induces a significant variation of the hydrogen bonding network near the surface of the aqueous solution.

On the other hand, the hydrogen bonding structure of adsorbed water on a solid substrate may control deposition nucleation, which is another pathway of heterogeneous ice nucleation. The hydrogen bonding structure may be affected by short and long range interactions between the substrate and the adsorbed water molecules. As a first approach, we have measured electron yield NEXAFS spectra of adsorbed water on graphite and titanium dioxide (TiO_2) under subsaturated conditions with respect to ice. Under isobaric conditions and by varying the temperature of the sample, we can change the relative humidity, which leads to varying amounts of adsorbed water in equilibrium between the substrate and water vapor. Preliminary results show that, under different relative humidity, the weakly and strongly coordinated OH bond of adsorbed water on TiO_2 and graphite show different contributions to the Auger electron yield NEXAFS spectrum, that is, the resonant transitions near the oxygen K-edge vary with relative humidity and temperature. We attribute this to the modification of the organization of water molecules in response to the interactions with the solid substrate. In view of the application of the NEXAFS technique, we believe it opens up a powerful tool to address the surface science of ice nucleation in the future.

Nucleation mechanism of oxocarboxylic acids involving hydration reaction: implications for the atmospheric models

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The formation of atmospheric aerosol particles is a dominant source of particulate matter, but the mechanism is ambiguous. In the clustering process, precursors with different reactivities can induce various chemical reactions besides the formation of hydrogen bonds. However, the clustering mechanism involving reactions is rarely considered in most of the nucleation process models. Oxocarboxylic acids are common compositions of secondary organic aerosol, but their roles in secondary organic aerosol formation is not fully understood. Glyoxylic acid (GA), the most abundant atmospheric oxocarboxylic acids, has been selected as an example of oxocarboxylic acids to study the clustering mechanism involving hydration reaction using Density Functional Theory combined with the Atmospheric Clusters Dynamic Code. The hydration reaction of GA can occur either in the gas phase or during the clustering process. In atmospheric conditions, the total conversion ratio of GA to its hydration reaction product (2,2-dihydroxyacetic acid) in both gas phase and clusters can be up to 85%, and the product can further participate in the clustering process. The differences in cluster properties induced by the hydration reaction lead to significant differences in cluster formation rates and pathways (Figure 1) at relatively low temperatures.

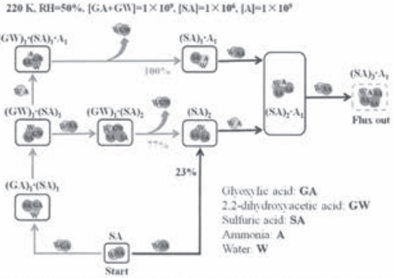

Figure 1. Main cluster formation pathways considering the hydration reaction of GA.

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