MUOAA 2024

Molecular-Level Understanding of Atmospheric Aerosols

April 1st – 5th 2024

Cargèse

Book of Abstracts

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Foreword

The Molecular-Level Understanding of Atmospheric Aerosols (MUOAA 2024) workshop and school gather scientists involved in studying atmospherically relevant aerosols at a fundamental level in the laboratory, in the field and via advanced modeling techniques (from molecules to global scales).

The objective of this event is to provide a forum where recent advances, and identified needs, in relation to the molecular understanding of aerosol properties are presented and discussed. In fact, predicting climate at both short and long-time scales, health impacts of bad air quality, require this scale of understanding as atmospheric aerosols are key players that influence these processes.

Challenges exist in understanding the formation of aerosol particles from gaseous precursors and the initial growth of these particles, the internal structure of aerosols, aerosol phase behavior, heterogeneous and multiphase (photo)chemistry, gas-surface interactions, the ability of aerosols to initiate ice and cloud nucleation, the evolution of aerosol optical properties, and the role of bioaerosols in the atmosphere.

These challenges cannot only be addressed through a dedicated and multidisciplinary approach, in which common awareness and interest is created and challenged across scientific fields and generation of scientists.

This is why we are holding the MUOAA workshop and school.

Attending this event will be an enriching experience for all participants, but particularly for graduate students and post-docs involved in fundamental aerosol research. The event provides a unique opportunity to meet many of the leading, international researchers in the field – both theoreticians and experimentalists – and to gain exposure to emerging analytical techniques.

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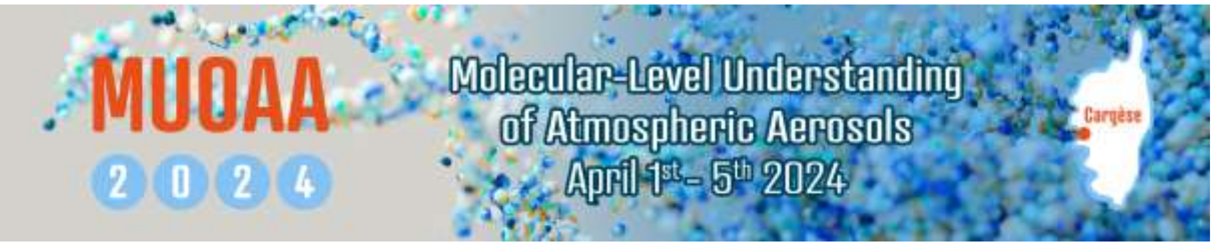
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Programme

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Molecular-Level Understanding of Atmospheric Aerosols

April 1st – 5th 2024

	Monday		Tuesday		Wednesday		Thursday		Friday
09:00	**Meeting opening George Christian**	09:00	**Summary of the previous day *by the students***	09:00	**Summary of the previous day *by the students***	09:00	**Summary of the previous day *by the students***	09:00	**Summary of the previous day *by the students***
09:15	Session Introduction: Garmash Olga	09:20	Session Introduction: George Christian	09:20	Session Introduction: Daële Veronique	09:10	Session Introduction: Garner Natasha	09:20	Session Introduction: Toubin Céline
09:20	**Laskin Alexander** *Molecular Insights into Atmospheric Brown Carbon: Optical Properties, Gas-Particle Partitioning, and Viscosity Assessment.*	09:25	**Ammann Markus** *The mystery of light induced reduction of nitrate in aqueous particles*	09:25	**Zimmerman Ralf** *Air pollution and health: Novel concepts for characterization of the toxicological impact and the organic composition of ambient aerosols and emissions*	09:15	**Rudich Yinon** *Transformations of biomass burning aerosol components and the effects on oxidative potential and cytotoxicity*	09:25	**Kurten Theo** *Peroxy radical recombination leads to an unexpectedly complex mixture of low-volatility products*
09:55	Schobesberger Siegfried *Retrieval of composition-resolved organic aerosol properties from thermal desorption measurements and inverse modeling*	10:00	Kong Xiangrui *Adsorbed Water Promotes Chemically Active Environments on the Surface of Sodium Chloride*	10:00	Berkemeier Thomas *Beyond Oxidative Potential: Multiphase Kinetic Modelling of Aerosol Health Effects*	09:50	Borduas-Dedekind Nadine *The production of singlet oxygen from brown carbon cooking organic aerosols (BrCOA) under indoor lighting.*	10:00	Besel Vitus *Generation of High-level Oxygenated Organic Molecule Data*
10:15	Coffee break	10:20	Coffee break	10:20	Coffee break	10:10	Coffee break	10:20	Coffee break
10:35	Nizkorodov Sergey *Approaching Quantified Volatility Distributions*	10:40	Krieger Ulrich *Iron-catalyzed Photochemical Degradation of Organics on Mineral Dust Aerosol Particles*	10:40	Reid Jonathan *Aerosol Particle Drying, Deposition and Resuspension*	10:30	Perraudin Emilie *Where and how to study SOA formation and ageing at the molecular level and on the field ?*	10:40	Louis Florent *In silico studies of the atmospheric reactivity of organic contaminants*
10:55	Khare Peeyush *Molecular-Level Chemical Composition of the Sources of Fine Airborne Particulate Matter in Two Megacities of North and South India*	11:00	Kiselev Alexei *Water on alkali feldspar: the role of crystalline structure, ion exchange, and the implication for atmospheric ice nucleation*	11:00	Wingen Lisa *Characterization of the Surface Layers of Organic Particles with Matrix Assisted Ionization in Vacuum-Mass Spectrometry (MAIV-MS) and a Little Magic*	10:50	Worsnop Doug *Atmospheric Aerosol Chemistry: Climate and Air Quality*	11:00	Wang Chia *Water Plays Multifunctional Roles in Formation of Secondary Organic Aerosols in Ozonolysis of Monoterpenes: A Combined VUV Photoelectron Spectroscopy, Mass Spectrometry and DFT Study*
11:10	Jie Chen *Ice Nucleation and Chemical Characteristics of Biomass Burning Aerosols Generated with Different Biomass Types and Burning Conditions*	11:20	Garner Natasha *Impact of Fe on the formation and aging of a-pinene secondary organic aerosol*	11:20	Joblin Christine *Interaction of PAH-based species in the gas phase with ultraviolet radiation*	11:10	Heinlein Laura Marie Dahler *Contribution of Particle Photooxidants to Winter Secondary Organic Aerosol Formation in a Subarctic City*	11:20	AbouHaidar Rawan *Reaction of Maleic Acid with Ozone at the Aqueous Interface*
11:25	Shahin Marwa *Gas-particle partitioning of xylene and naphthalene oxidation products: temperature and NOx influence*	11:35	Eliet Sophie *TeraHertz spectroscopy for aerosols studies*	11:40	Group Discussion	11:25	Gerritz Lena *Mechanistic Insight into Radical Formation During the Photochemical Aging of Secondary Organic Aerosols*	11:35	Wang Pengcheng *Gas-phase kinetics of Criegee intermediate reactions with implications for aerosol formation in the atmosphere*
11:40	Group Discussion	11:50	Group Discussion			11:40	Group Discussion	11:50	Group Discussion
	Lunch		**Lunch**		**Lunch**		**Lunch**		**Lunch**
14:00	Session Introduction: Boréave Antoinette	14:00	Session Introduction: Meroni Cesare	14:00	**Excursion**	14:00	Session Introduction: Angelaki Maria	14:00	Session Introduction: Villenave Éric
14:05	**Prisle Nonne** *Water - the dark matter of atmospheric aerosols*	14:05	**Monod Anne** *Atmospheric multiphase chemistry of organic species*			14:05	**Signorell Ruth** *Accelerated and unexpected in-particle chemistry*	14:05	**Abbatt Jonathan** *Multiphase Oxidation Chemistry in Indoor and Wildfire-Impacted Environments*
14:40	Ault Andrew *Dropping Acid in the Atmosphere: Does It Matter for Secondary Organic Aerosol?*	14:40	Raff Jonathan *Hidden Complexities of Chromophore Photochemistry in Aerosol Aging and Heterogeneous Nitrogen Oxide Chemistry*			14:40	Jones Stephanie *Determination of the viscosity and surface tension of levitated droplets at supercooled temperatures*	14:40	Bilde Merete *Properties of secondary organic aerosol from oxidation of monoterpenes at different temperatures*
15:00	Kleinheins Judith *Effect of surface tension on aerosol particle critical supersaturation: a bottom-up modelling study*	15:00	Petersen-Sonn Emma Amalie *Excited triplet states from aerosol extracts competing with OH radical and singlet oxygen*			14:55	Hoffman Thorsten *Chemistry in nanometer aerosol particles: Flow tube experiments with Diels-Alder reactions as a model system*	15:00	Pouyes Pauline *Limits of the molecular tracer approach in the understanding of SOA formation and fate processes*
15:15	Coffee break	15:15	Coffee break			15:15	Coffee break	15:15	Coffee break
15:35	Koop Thomas *Experimental studies on the activity of molecular ice nucleators*	15:35	Angelaki Maria *Spontaneous H2O2 formation at the interfaces of salt-containing aqueous droplets: A mechanistic study*			15:35	David Gregory *Sea-salt hygroscopicity and crystallization of their mixture with oxalic acid*	15:30	Kenseth Christopher *Particle-Phase Accretion Forms Dimer Esters in Pinene Secondary Organic Aerosol*
15:55	Bzdek Bryan *Surface-Area-to-Volume Ratio Determines Surface Tensions in Microscopic, Surfactant-Containing Droplets*	15:50	Sobanska Sophie *Molecular-scale view of the interaction of water and ice with organic species of atmospheric interest*			15:55	Meroni Cesare *Investigation of the Spontaneous Formation of Molecular Iodine at the Air/Water Interface with Optical Tweezers*	15:45	Gratien Aline *Molecular composition of secondary organic aerosol using chromatography and mass spectrometry*
16:15	Freedman Miriam *The role of surface features in promoting heterogeneous ice nucleation*	16:10	Garmash Olga *Molecular cluster composition and aerosol formation over Siberian boreal forest*			16:10	Bain Alison *Investigating the Dynamic Surface Composition of Aerosol Droplets*	16:05	Perraud Veronique *Impact of carbon storage technology alkanolamines on new particle formation in air*
16:35	Lin Jack *Concentration profiles of an organosulfate surfactant in a liquid microjet*	16:25	Prophet Alex *Oxidation of Ions at the Air-Water Interface: Towards a General Classification of Surface and Bulk Reaction Kinetics in Aerosol*			16:30	Wallace Brandon *Accelerated Keto-Enol Tautomerization of Aqueous Malonic Acid in Micron-Sized Oil Emulsions*	16:25	Zhang Yue *Quantifying the Mass Loading, Aging, and Cloud Properties of Polystyrene Nanoplastic Particles in the Atmosphere*
16:50	Group Discussion	16:40	De La Puente Miguel *Neural-Network-based Simulations of Acidity at the Surface of Aqueous Aerosols*			16:45	Group Discussion	16:45	Group Discussion
		16:55	Group Discussion						
17:05		17:10	Poster Session			17:00	Poster Session	17:00	Conclusion & Evaluation
19:00	**Welcome Cocktail**			19:00	**Dinner at the port**	19:00	**BQQ at the Institute**		

Abstracts - Oral

Molecular Insights into Atmospheric Brown Carbon: Optical Properties, Gas-Particle Partitioning, and Viscosity Assessment.

Alexander Laskin[*]

Department of chemistry, Purdue University, West Lafayette, IN 47907, USA.

Key words: brown carbon, molecular characterization, high-resolution mass spectrometry

Abstract: Biomass burning organic aerosol (BBOA) is a major source of 'brown carbon' in the atmosphere, and the chemical composition and properties of brown carbon within these aerosols can vary depending on factors such as the type of biomass burned, combustion conditions, and atmospheric ageing. Molecular characterization of BBOA using advanced methods of high-resolution mass spectrometry provides essential insights into the composition, properties, and behavior of atmospheric brown carbon, contributing to a more comprehensive understanding of its environmental impacts. These studies have enabled the identification and quantification of specific components of BBOA, including strongly absorbing chromophores, such as phenolic, quinone and nitroaromatic compounds, N-heteroatom compounds, polycyclic aromatic hydrocarbons, etc. Through comprehensive understanding the chemical composition of brown carbon, we can now assess its sources and atmospheric transformations. Recent investigations have also broadened their scope to explore the partitioning of brown carbon species between the particle and gas phases. These measurements yield valuable data on particle-to-gas transition enthalpies and apparent volatilities of individual BBOA species, crucial for constructing volatility basis sets (VBS). The resulting VBS distributions enable an assessment of equilibrium gas-particle partitioning across various atmospheric conditions of organic mass loadings, temperatures, and pressures. under conditions relevant to Earth's atmosphere, encompassing a broad range of total organic mass loadings and temperatures. Furthermore, novel parameterization models leverage chemical characterization and volatility datasets to evaluate the viscoelastic properties of BBOA. This comprehensive molecular understanding of BBOA chemistry is essential for predicting their ability to undergo chemical reactions, partition between gas and particle phases, and impact atmospheric environment and related processes, such as radiative forcing of climate and cloud formation. This presentation will provide an overview of recent advancements in this field and outline future directions for continued research.

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Retrieval of composition-resolved organic aerosol properties from thermal desorption measurements and inverse modeling

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Key words: organic aerosol, mass spectrometry, volatility, desorption modeling, thermal decomposition

Abstract: Using the filter inlet for gas and aerosols (FIGAERO), coupled to a chemical ionization mass spectrometer, the composition of a major fraction of an organic aerosol sample can be measured through temperature-controlled evaporation followed by soft ionization of desorbed molecules and the mass spectrometric detection and identification of the resulting ions. A so-called thermogram is obtained for each ion: signal vs. desorption temperature. Each thermogram is thus determined by the thermal desorption behavior of the respectively detected molecule, i.e., in principle, by its effective volatility.

FIGAERO has been gaining wide-spread use in both lab and field applications. But it remains a challenge to interpret the measured thermograms for quantitatively retrieving thermodynamic properties such as vapor pressures, vaporization enthalpies, decomposition kinetics and effects of non-ideal mixing and possibly phase separation.

I will present recent advances we made in understanding the FIGAERO measurement process by explicit kinetic modeling, from model compounds to realistic secondary organic aerosol. Our inverse modeling approach performs extremely well in explaining calibration experiments, even spanning ten orders of magnitude in vapor pressure. Conversely, that approach amounts to the determination of hitherto unknown vapor pressures of low-volatility species (here: high-order polyethylene glycols). More generally, however, we have observed unexpectedly large variability in the effective volatilities of organic species upon entering even simple mixtures and/or upon photochemical aging. We investigated such variabilities through targeted experiments, including modified measurement protocols that add an isothermal desorption step at controlled humidity. Model simulations were then used to interpret the observed variabilities and to quantify and constrain underlying molecular properties and processes, e.g., vapor pressures, enthalpies, condensed-phase reactions, and activity coefficients.

Recent efforts have focused on levoglucosan, a major semi-volatile organic produced in the combustion of cellulose and hence a widely used marker compound for biomass burning. We have also proceeded in constraining instrumental artifacts in the measurement data due to non-ideal transport into the detector, and we explored efficient optimization algorithms to fit model parameters to large datasets, as actual organic aerosols consist of and desorb into hundreds of individual compositions.

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Atmospheric Transformations of Organic Aerosol Emitted from Burning of Biomass and Urban Materials

Sergey A. Nizkorodov

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Key words: *wildland-urban interface; biomass burning; photodegradation; composition*

Abstract:

Large-scale forest fires significantly contribute to the atmospheric burden of organic aerosol (OA). Wildfire events increasingly occur at the wildland-urban interface (WUI), burning not only biomass but also a wide range of urban materials. The chemical composition and properties of OA from WUI fires are poorly characterized. This presentation will discuss the mass absorption coefficients (MAC), chemical composition, and photochemical aging of OA from pyrolysis and smoldering of common urban materials. OA samples were collected and aged by exposing them to simulated solar radiation directly on the Teflon filter collection substrates. The MAC values of the unaged and aged OA were measured by spectrophotometry after extracting OA in suitable solvents or directly on optical substrates. The samples were analyzed using ultrahigh pressure liquid chromatography photodiode array high resolution mass spectrometry (UPLC-PDA-HRMS) with either atmospheric pressure photo ionization (APPI) and electrospray ionization (ESI) to ensure detection of both polar and nonpolar OA components. The samples were further investigated using temperature programed desorption (TPD) stage interfaced with direct analysis in real time (DART) ionization source to assess volatilities of prominent individual species in OA. We find that that MAC values range over an order magnitude depending on the material. Exposure to solar radiation can either reduce MAC (photobleaching) or increase it (photoenhancement), reflecting complex aging mechanisms driven by condensed phase photochemical reactions in OA. The OA samples contain a number of unique compounds that can be used as markers of WUI fires, including metal complexes and halogen-containing compounds.

Molecular-Level Chemical Composition of the Sources of Fine Airborne Particulate Matter in Two Megacities of North and South India

Peeyush Khare[1,*], Yufang Hao[1], Vishnu Murari[2], Sreenivas Gaddamidi[2], Jens Top[1], Marianne Gosselin[1], Tianqu Cui[1], K.V. George[3], Manousos-Ioannis Manousakas[1], Ashutosh Shukla[2], Lu Qi[1], Dongyu Wang[1], Jean-Luc Jaffrezo[4], Jay Slowik[1], S.N. Tripathi[2], Kaspar R. Daellenbach[1], André S.H. Prévôt[1]

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Key words: *Organic aerosol, biomass burning, oxidative potential, mass spectrometry, source apportionment.*

Abstract :

Exposure to fine airborne particulate matter claims over 1 million lives each year in India making it one of the worst affected regions in the world. Regulatory policies are severely restricted by a limited understanding of urban sources and their relative contributions to poor air quality. Detailed chemical speciation of airborne particulate matter is required to identify sources and enact effective control strategies. We collected multi-season filter samples from two select megacities of India – Lucknow (in the north) and Pune (in the south), which exhibit large seasonal variations and are impacted by a diversity of anthropogenic and biogenic sources. The water-soluble organic mass (WSOM) of the samples was analyzed using offline time-of-flight aerosol mass spectrometry (LTOF-AMS), extractive electrospray ionization (EESI)-ToF-MS and total organic carbon analyzer. The elemental composition, inorganic ions, organic tracers and oxidative potential were also measured separately. Subsequently, sources were identified via advanced source apportionment techniques. Lucknow showed significantly higher wintertime WSOM concentrations than Pune that exceeded WHO safe limits by a factor of 15-20. The high concentrations were driven by primary biomass burning sources dominated by levoglucosan and reduced nitrogen-containing organic species whose contributions doubled from day- (18%) to night-time conditions (40%). This indicated prominence of local sources in Lucknow, which were not observed in Pune. Wintertime aged source contributions were also observed in both cities that correlated with tracers of biomass burning (e.g., mannosan, galactosan, vanillic acid) suggesting influence of regional sources. Biogenic sources were more important during summer constituting 50-60% of the WSOM in both cities. The biogenic factor was dominated by oxygenated species containing C10-C15 carbons with O:C and H:C ratios of 0.2-0.3 and 1.5-1.7, respectively, indicating monoterpenes- and sesquiterpenes-based sources. Furthermore, anthropogenic contributions from sulfur-containing sources correlated with selenium, methanesulfonic acid and 4-methylphthalic acid. All identified sources were correlated with measured oxidative potential via multilinear regression approaches to assess their relative importance for health impacts, thus enabling formulation of effective air pollution control policies in the region.

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Ice Nucleation and Chemical Characteristics of Biomass Burning Aerosols Generated with Different Biomass Types and Burning Conditions

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Key words: Biomass Burning Aerosol, Ice Nucleation, Photochemical Aging

Abstract: Biomass burning aerosol (BBA) from domestic heating and global forest fires significantly contributes to the global aerosol burden and the associated radiative forcing. However, the physicochemical properties and ice nucleation activities (INAs) of BBA are very heterogeneous, impeding its representation in aerosol and climate models through universal parameterizations. This uncertainty arises partly due to the heterogeneity in biomass sources and the complex atmospheric aging of BBA after its emission. This study comprehensively investigates the INAs of BBA generated through laboratory-controlled burns with different biomasses (wood, peat and leaf) and burning conditions (flaming and smoldering phases). Simultaneously, the BBA was systematically characterized using a combination of online and offline techniques, including analyses of BBA bulk-phase and single-particle compositions, providing elaborate information on its chemical natures. BBA produced from different processes exhibits distinct and reproducible chemical compositions, with carbonaceous materials being the dominant components. In contrast, their INAs show substantial variability under mixed-phase cloud conditions and have no correlations with the chemical variables associated with carbonaceous material, suggesting that carbonaceous components cannot predict the INAs of BBA. Photochemical aging under atmospheric relevant conditions increases the oxidation state and alters the organic content of BBAs, but its impact on their INAs is inconsistent across experiments. When evaluating the INAs of produced BBA under atmospheric-relevant particle concentration and size conditions, we found its influence on immersion freezing of cloud droplets is negligible. The limited INAs of BBAs observed in this study cannot explain the considerable concentration of ice nucleating particles (INPs) detected by field studies during BBA pollution. This discrepancy is likely attributed to the absence of mineral-containing particles in BBAs produced under our laboratory conditions, such as the lofted ash and soil particles that can be prevalent in real atmospheric burning events. We propose conducting studies on the INA of BBA with specific identification of its mineral phase, to further evaluate its contribution to the atmospheric INP populations.

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Gas-particle partitioning of xylene and naphthalene oxidation products: temperature and NO_x influence

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Key words: SOA, gas-particle partitioning, CHARON-PTR-ToF-MS, aerosol flow reactor

Abstract: Aromatic hydrocarbons (AHs) are an ubiquitous class of volatile organic compounds (VOCs) containing at least one aromatic function. VOCs react with atmospheric oxidants, forming reaction products of lower vapor pressure, also known as semi- and intermediate-volatile organic compounds (SVOCs and IVOCs) [1]. A key process determining the fate of the IVOCs and SVOCs is their ability to partition between gas and particle phases forming secondary organic aerosols (SOA). Due to the lacking of chemical specificity of oxidation products and the influence of environmental conditions, SOA is not yet satisfactorily constrained by atmospheric models, resulting in large uncertainties in their production [2,3].

The aim of this study is to evaluate gas particle partitioning of S/IVOCs involved in SOA formation from the photooxidation of AHs under different conditions. For that purpose, the photooxidation of two AH models was investigated in an oxidation flow reactor (OFR), a monoaromatic (m-xylene) and a polyaromatic (naphthalene) Compounds. A CHARON (CHemical Analysis of aeRosol ON-line) was deployed and coupled to a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) to alternatively measure gas and particle phase chemical composition at molecular level. Experiments have been conducted at different environmental conditions: 5 and 20 °C, at both low and high VOC/NO_x ratios.

From all experiments, SOA yields ranged from 8 to 43 %. For each model precursor, we identified more than 150 compounds. In the xylene system, gas phase compounds were dominated by $C_{3,5,8}H_yO_{1-4}$ while particle phase was more oxidized and dominated by $C_{6-8}H_yO_{3-6}$ (Figure 2.). The C_8 compounds are dominating in both gas (26%) and particle phases (25%) compared to the other carbon classes. The most abundant C_8 compound in gas phase was tolualdehyde ($C_8H_8O.H^+$ at m/z 121.06), representing alone 16% of the identified reaction products. Other major C_8 products are nitrogen-containing compounds, such as nitroxylene $(C_8H_9NO_2)H^+$ at m/z 152.07.

As for naphthalene, the dominant oxidation products were C_{10} compounds notably naphthoquinone $(C_{10}H_6O_2)H^+$ at m/z 159.04 and formyl-cinnamaldehyde $(C_{10}H_8O_2)H^+$ at m/z 161.06. Other major products include the C_9 coumarin $(C_9H_6O_2)H^+$ at m/z 147.05 and the C_8 phthaldialdehyde $(C_8H_6O_2)H^+$ at m/z 135.05.

Among all species, approximately 35-53% of the detected ions in the particle phase partition also in the gas phase allowing the evaluation of their partitioning, while the remaining fraction is found in the condensed phase only. The effect of temperature on partitioning will be discussed through this presentation.

Acknowledgements

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Water - the dark matter of atmospheric aerosols.

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Key words: *Mixed aerosols; aerosol-water interactions; surface activity; surface properties*

Abstract: Atmospheric aerosols are typically mixtures of both organic and inorganic species. In addition, ubiquitous atmospheric water constantly interacts with aerosols and may critically influence their formation, physical and chemical properties, and ultimate fate. Water vapor is the most abundant atmospheric trace gas, but concentrations show strong temporal and spatial variation. Furthermore, interactions of water with atmospheric aerosols often result in highly non-ideal mixtures (Prisle et al., 2010). Therefore, the influence of water on the physics and chemistry of atmopheric aerosols is often poorly constrained.

Many organic components of atmospheric aerosols are surface active in aqueous solution. In aqueous aerosols and droplets, surface adsorption lead to enhanced surface concentrations compared to the (interior) bulk, but can also strongly deplete the bulk phase due to the very high surface area (A) to bulk volume (V) ratio in sub-micron size ranges. This effect can be so strong that aerosol or droplet size and resulting A/V becomes the determining factor for surface tension (Bain et al., 2023). The surface tension may in turn impact a wide range of physical and chemical properties of aqueous aerosols and droplets (Prisle, 2024). Organic aerosols also include numerous species with Brønsted acidic or basic character. The concentrations of acidic or basic species affect aerosol pH, which in turn influences the protonation state of individual acidic or basic aerosol components. The contribution of organic aerosol acid-base dissociation on aerosol H^+ concentration is often overlooked in atmospheric models, but can significantly impact aqueous aerosol chemistry, sulfate mass formation, and predicted cloud radiative effect (Sengupta et al., 2024). When organic aerosols are simultaneously surface active and Brønsted acidic or basic, the effects of water interactions are complex and non-linear, in particular as the dissociation state of acids and bases at the aqueous surface may deviate strongly from that in the bulk (Prisle, 2024).

We have recently found that water can be taken up to aerosol surfaces at extremely low ambient humidities, much below the deliquescence point or any measurable hygroscopic growth (Lin et al., 2021). In these nano-confined surface layers, water can mobilize and lead to seggregation of ions, and even catalyze chemical transformations. We have also found several examples of how non-ideal water interactions can lead to previously unrecognized perturbations in the composition and morphology of laboratory-generated aerosols, potentially biasing decades of aerosol process studies (Rissler et al., 2023).

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation programme (project SURFACE, grant agreement no. 717022) and the Research Council of Finland (grant nos. 257411, 308238, 314175, 335649, and 351476).

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Dropping Acid in the Atmosphere: Does It Matter for Secondary Organic Aerosol?

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Key words: *Aerosol Acidity ; Secondary Organic Aerosol ; Acid Dissociation ; Spectroscopy ; Mass Spectrometry*

Abstract: Isoprene has the highest atmospheric emissions of any non-methane hydrocarbon, and isoprene epoxydiols (IEPOX) are well-established oxidation products and the primary contributor forming isoprene-derived secondary organic aerosol (SOA). Highly acidic particles (pH 0-3) widespread across the lower troposphere enable acid-driven multiphase chemistry of IEPOX, such as epoxide ring-opening reactions forming methyltetrol sulfates through nucleophilic attack of sulfate (SO_4^{2-}). Herein, we systematically demonstrate an unexpected decrease in SOA formation from IEPOX on highly acidic particles (pH < 1). While IEPOX-SOA formation is commonly assumed to increase at low pH when more [H^+] is available to protonate epoxides, we observe maximum SOA formation at pH 1, and less at pH 0.0 and 0.4. This is attributed to limited availability of SO_4^{2-} at pH values below the acid dissociation constant (pKa) of SO_4^{2-} and bisulfate (HSO_4^-). The nucleophilicity of HSO_4^- is 100× lower than SO_4^{2-}, decreasing SOA formation and shifting particulate products from low-volatility organosulfates to higher-volatility polyols. Current model parameterizations predicting SOA yields for IEPOX-SOA do not properly account for the SO_4^{2-}/HSO_4^- equilibrium, leading to overpredictions of SOA formation at low pH. Accounting for this underexplored acidity-dependent behavior is critical for accurately predicting SOA concentrations and resolving SOA impacts on air quality.

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Effect of surface tension on aerosol particle critical supersaturation: a bottom-up modelling study

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Abstract

Organic substances in the atmosphere can lower the surface tension (ST) of atmospheric aerosol particles below the value of pure water, thereby affecting the particles' ability to serve as cloud condensation nuclei (CCN). Due to the complex composition of atmospheric aerosol particles, a complete picture of the importance of ST reduction for CCN activation is still lacking. Previously, we tested the ability of common binary ST models to fit experimental ST data of a broad range of aqueous mixtures containing salts and amphiphilic surfactants (Kleinheins et al., 2023). We found that, among others, the simple Eberhart model (Eberhart, 1966) could accurately reproduce ST isotherms for all studied substance types.
Our current study has two goals: (i) to develop an accurate model for the ST of multicomponent aqueous mixtures, and (ii) to apply this ST model in the calculation of aerosol particles' critical supersaturation (Scrit).

Firstly, we derived a multi-component version of the Eberhart model based on previously established mathematical relationships (Shardt et al., 2021). By adding a simple empirical function to account for salting-out effects, we successfully fit ternary ST data of mixtures containing water and two of the following: an organic substance, a salt, or a surfactant. We also successfully predicted the ST of a quaternary mixture (water–surfactant–organic–salt), which, to our knowledge, has not been achieved before.
Secondly, we explored the impact of ST reduction and the way it is modelled on Scrit. In small particles having a high surface-to-volume ratio, solute molecules partition to the surface, leading to significant depletion from the bulk volume of the particle. We thus combined the new Eberhart model with the "monolayer model" by Malila & Prisle (2018) that allows for a calculation of the bulk depletion. If bulk depletion is incorrectly assumed to be negligible, the predicted Scrit is significantly lower than if bulk depletion is correctly accounted for. Moreover, the predicted Scrit considering surface tension reduction and bulk depletion is similar to the Scrit predicted when neglecting all surface partitioning related effects (classical Köhler theory), showing that a substantial fraction of the ST effect is compensated when accounting for bulk depletion.

Keywords: surface tension, surface composition, Köhler theory, bulk, surface, partitioning, bulk depletion, Raoult, Kelvin, critical Supersaturation

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*Speaker

Experimental studies on the activity of molecular ice nucleators

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Key words: Ice nucleation; molecular ice nucleator; microfluidic device

Abstract: Ice nucleation is important for the formation of ice clouds and the initiation of precipitation. In the past, there have been extensive studies on various heterogeneous ice nucleators, both in laboratory experiments as well as in the field or on field-collected samples. The majority of these studies are concerned with particulate ice nucleators, but in recent years it has become clear that also ice nucleators of molecular origin can catalyze ice nucleation. However, a detailed molecular understanding of their way of action is still lacking and, hence, dedicated experiments towards that goal appear essential.

Therefore, we investigated several naturally occurring and synthetic substances, of which some are of atmospheric relevance. For this purpose, we applied two setups for detecting droplet freezing. First, the BINARY (Bielefeld Ice Nucleation ARraY) setup employing microliter-volume droplets and, secondly, the recently developed nanoBINARY (nanoliter Bielefeld Ice Nucleation ARraY) setup, which is a microfluidic device employing nanoliter-volume droplets. In combination, these two devices allow for studying freezing processes over a wide temperature range from the ice melting point down to the homogeneous ice nucleation limit of water droplets. The latter ability is an important prerequisite for studying molecular ice nucleators, which often induce heterogeneous ice nucleation only at low temperature close to the homogeneous ice nucleation limit.

We will present data on ice nucleation induced by molecules of natural as well as synthetic origin, including antifreeze proteins, ice-nucleating proteins, polysaccharides as well as monomers, oligomers and polymers of poly(vinyl alcohol). Together these data strongly suggest that the ice nucleation temperature within one class of molecules scales with molecular size: the larger the size of a molecular ice nucleator, the higher its ice nucleation temperature.

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Surface-Area-to-Volume Ratio Determines Surface Tensions in Microscopic, Surfactant-Containing Droplets

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Key words: *surface tension, droplet, optical tweezers, interface, aerosol*

Abstract: The surface composition of aerosol droplets is central to predicting cloud droplet number concentrations, understanding atmospheric pollutant transformation, and interpreting observations of accelerated droplet chemistry. Due to the large surface-area-to-volume ratios of aerosol droplets, adsorption of surfactant at the air–liquid interface can deplete the droplet's bulk concentration, leading to droplet surface compositions that do not match those of the solutions that produced them. Through direct measurements of individual surfactant-containing, micrometer-sized droplet surface tensions, and fully independent predictive thermodynamic modeling of droplet surface tension, we demonstrate that, for strong surfactants, the droplet's surface-area-to-volume ratio becomes the key factor in determining droplet surface tension rather than differences in surfactant properties. For the same total surfactant concentration, the surface tension of a droplet can be >40 mN/m higher than that of the macroscopic solution that produced it. These observations indicate that an explicit consideration of surface-area-to-volume ratios is required when investigating heterogeneous chemical reactivity at the surface of aerosol droplets or estimating aerosol activation to cloud droplets.

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2024 MOUAA Abstract

The role of surface features in promoting heterogeneous ice nucleation

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Aerosol particles catalyze ice nucleation in the atmosphere, which allows ice to form at temperatures above – 38 degrees C. While the surface features of interest for the promotion of ice nucleation are known, their relative importance is not, and as a result, we cannot predict the ice nucleation activity of a given type of aerosol particles. To determine how the surfaces of aerosol particles facilitate the ice nucleation process, we have studied synthetic systems with atmospheric relevance in which we can continuously tune surface features. This talk will give several examples of my group's work in this area. I will then focus on recent work investigating the impact of dopants on ice nucleation using magnesium and zinc aluminate spinel oxides, as well as ongoing work on the ice nucleation activity of fresh and aged microplastics. Our studies have allowed us to make general conclusions about the importance of crystallinity, lattice spacing, pore size, and functional groups through numerous studies across multiple systems, which will eventually allow us to predict the ice nucleation activity of aerosol particles based on their composition and structure.

Concentration profiles of an organosulfate surfactant in a liquid microjet

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Key words: Aqueous solutions; Bulk/surface partitioning; Droplets; X-ray photoelectron Spectroscopy

Abstract: The atmosphere contains many surface-active compounds that preferentially adsorb to the surfaces of droplets. At the droplet surface, these compounds may depress the aqueous surface tension as well as deplete the droplet bulk concentration. These two processes have opposing impacts on cloud droplet formation. The delineation between droplet surface and bulk is unclear. Theoretical frameworks that exist to model bulk/surface partitioning in aqueous droplets can be broadly divided into those that treat the surface as a Gibbs' dividing surface or as a physical layer or layers. Multilayer surface models are rare, and no models are currently able to account for an extended transition region between the surface and the bulk.

X-ray photoelectron spectroscopy (XPS) has emerged as a powerful tool capable of providing direct and chemically specific measurements of aqueous surfaces. In this work, we take advantage of the high photon flux and photon energies at the HIPPIE beamline at the MAX IV Laboratory, which allows us to probe several nanometers below the aqueous surface. Solutions containing sodium chloride ($NaCl$) and sodium dodecyl sulfate (SDS), a strongly surface-active compound used as a model organosulfate, were studied as a liquid microjet ($d = 20\ \mu m$) using XPS. Spectra for the sodium, chlorine, carbon, sulfur, and oxygen core level orbitals were measured at five different depths below the aqueous surface. Concentrations derived from the XPS spectra reveal three distinct regions: a surface layer at the lowest probing depth (~1 nm), an intermediate layer at the two intermediate probing depths (~2-3 nm), and the deepest layer at the lowest probing depth (~4 nm). These results have important implication for how we understand the extent of bulk/surface partitioning in atmospheric aqueous droplets.

We acknowledge MAX IV Laboratory for time on Beamline HIPPIE under Proposal 20180417. Research conducted at MAX IV, a Swedish national user facility, is supported by the Swedish Research Council under contract 2018-07152, the Swedish Governmental Agency for Innovation Systems under contract 2018-04969, and Formas under contract 2019-02496. The research leading to this result has been supported by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme, Project SURFACE (Grant Agreement No. 717022). The authors also gratefully acknowledge the financial contribution from the Academy of Finland, including Grant Nos. 290145, 308238, 314175, 331532, and 335649.

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The mystery of light induced reduction of nitrate in aqueous particles

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Key words: nitrate photolysis, biomass burning, photosensitizer, surface enhancement

Abstract: Light-induced production of NOx from nitrate containing particles has been well documented from numerous laboratory and field measurements. Since photolysis of nitrate in solution is rather slow, it has been suggested that photolysis of particle phase nitrate or nitric acid may occur at enhanced rates. Suggested reasons mostly concentrate on an enhanced quantum yield due to a reduced solvent cage at the interface and in parallel on the speculation that nitrate ions may occur preferentially at surfaces. However, X-ray photoelectron spectroscopy experiments have demonstrated that nitrate is rather depleted from the interface in more dilute aqueous solutions. Though, cooperative effects may be in place that may change that via ion-pairing or preferential solvation with surface active organics, which call for dedicated investigations of the surface propensity and local environment of nitrate ions in complex aqueous solutions. We will present preliminary XPS and resonant Auger-Meitner electron spectroscopy experiments that indicate the sensitivity of the electronic structure of nitrate to the local environment. A second line of hypotheses to explain photochemical reduction of nitrate is via photosensitized pathways. Chromophores for those are abundant in the atmosphere, especially also including brown carbon contained in biomass burning aerosol. Along that line we performed experiments with iron(III)citrate, dihydroxybenzaldehyde, benzophenone, methylene blue and authentic biomass burning aerosol extracts. These clearly demonstrate NOx emission driven by the organic chromophores.

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Adsorbed Water Promotes Chemically Active Environments on the Surface of Sodium Chloride

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Abstract

Gas-particle interfaces are known for their chemical activity, particularly when they interact with adsorbed water. This interaction is crucial as it can facilitate thermodynamic reactions that are typically unlikely, such as spontaneous reactions on salt surfaces when they are solvated by adsorbed water. Salts, particularly chloride salts like NaCl, are widely found on Earth and other planets and exhibit unique properties and chemical reactivities. However, our comprehensive understanding of these properties is still evolving. NaCl, in particular, plays a significant role in Earth's climate. Due to its high hygroscopicity, it contributes to aerosol growth and, consequently, cloud formation. In its dry, crystalline form, NaCl is generally inert, except at its surface, where it can react with nitrogen oxides. This reactivity becomes especially relevant considering that the NaCl surface begins to bind with water at relatively low humidity levels.

This study investigates the chemical interactions at gas-particle interfaces, focusing on how NaCl surfaces react with SO2. The study uses a blend of experimental techniques and theoretical models, including a comparison with NH4Cl to assess the impact of different cations. The findings reveal that NaCl surfaces rapidly transform into Na2SO4 and release a new chlorine component when exposed to SO2 in low-humidity conditions. In contrast, NH4Cl surfaces show limited SO2 absorption and minimal change. Further analysis through depth profiling demonstrates the altered layers and specific elemental ratios at the surfaces of the crystals. The study identifies that the chlorine species detected are expelled from the NaCl crystal structure. This conclusion is supported by detailed atomistic density functional theory calculations. Additionally, molecular dynamics simulations bring to light the dynamic and chemically active environment of the NaCl surface, influenced significantly by an intense interfacial electric field and the presence of water layers, even in trace amounts.

Overall, these insights emphasize the unique chemical activities of salt surfaces and the surprising chemical reactions that can occur due to their interaction with interfacial water, highlighting the complexities of such interactions even in relatively dry conditions.

Keywords: Sulfate, Surface Chemistry, Interface, Salt, Ionic Strength

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[*] Speaker

Iron-catalyzed Photochemical Degradation of Organics on Mineral Dust Aerosol Particles

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Key words: Mineral dust, iron-catalyzed photochemistry, heterogeneous processing

Abstract: Iron is known to catalyze the photochemical degradation of organic matter, and it is almost ubiquitous in mineral dust aerosol particles. This study uses single, levitated aerosol particles containing various mineral dusts to investigate the photochemical degradation (illumination wavelength: 473 nm) of organics using citric acid as a proxy compound. Rapid and very significant mass loss of citric acid (up to 80 % of initial organic mass) was observed for many of the dust-containing particles, which we attribute to photochemical reactions with iron as a catalyst. We measured this using immersions of four iron-containing samples: two natural samples representing very iron-poor and iron-rich clay minerals (KGa-2 Kaolinite, high defect, from Warren County, Georgia, USA; CCa-2 Chlorite, from Flagstaff Hill, El Dorado County, California, USA), Arizona Test Dust (ATD, with an iron concentration between CCa-2 and KGa-2), and for comparison pure Fe_2O_3 nanopowder (<50 nm particle size).

We present evidence for two pathways of iron-catalyzed photochemical processing, homogeneous and heterogeneous, namely through iron leached from dust particles or residing on dust particle surfaces. In view of the variety of iron(III) oxide-containing particles investigated here, it can be assumed that these mechanisms can be expected occur ubiquitously in the atmosphere. While these mechanisms are not expected to affect the global budget of organic species in the atmosphere, they result in reducing the thickness of organic coatings acquired by air-borne mineral dust via condensation of secondary organic components. This may enhance the ability of mineral dust aerosol particles to act as ice-nucleating particles (INPs).

Water on alkali feldspar: the role of crystalline structure, ion exchange, and the implication for atmospheric ice nucleation

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Key words: atmospheric ice nucleation; mineral dust aerosol; alkali feldspar; water at interfaces; ion exchange.

Abstract: Due to its ubiquitous presence in the Earth's crust, alkali feldspar is an important constituent of airborne mineral dust, thus strongly affecting formation of atmospheric ice particles. The presence of ice particles in the atmosphere is important for a variety of processes such as radiative heat transfer, formation and evolution of clouds and precipitation, and absorption of trace gases. Some alkali feldspars have particularly high ice nucleation (IN) activity. This phenomenon has been recently ascribed to structural similarities of the ice (10-10) prism planes and the (100) planes of alkali feldspar. However, since the (100) plane does not exhibit crystallographic match to Ih ice, a layer of hydroxyl groups on the surface of feldspar is required to minimize the interfacial energy and thus create beneficial conditions for ice nucleation. The structure of this hypothetical hydroxyl layer under realistic environmental conditions is not known and has to be derived from measurements.

This study combines the UHV IR Reflection Absorption Spectroscopy (IRRAS), the X-ray photoemission spectroscopy (XPS), and the Auger electron yield near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the oxygen K-edge to investigate the structure of water adsorbed on the (001) and (010) planes of alkali feldspar. We compare the IRRAS spectra of D_2O adsorbed on the surface of two distinctly different K-feldspar specimen: gem-quality K-rich orthoclase and structurally complex microcline perthite, varying the amount of adsorbed water and deposition temperature in the range between 118 K and 250 K. By characterizing the ice nucleation from water vapor (i.e., deposition mode nucleation) at cold temperatures (118 - 150 K) on a range of K-feldspar samples, we find direct evidence that ice nucleation efficiency of K-feldspar samples is related to the structural symmetry and orientation of crystalline facets.

We further combine XPS with NEXAFS to probe the feldspar samples under dry (0.1 % RH) and humid (50% RH) atmosphere at room temperature for both untreated samples and after immersing them in water, to probe the hydrogen bonding structure of ice in the presence of ions, released from the sub-surface mineral framework. We show that the exchange of K+ ions with H3O+ apparently inhibits the formation of tetrahedrally coordinated water upon adsorption on the sample surface. In other words, the presence of ions makes water structure more "liquid-like". The interpretation of spectroscopic results is supported by direct measurements of the IN efficacy of feldspar specimens performed in a droplet freezing array setup.

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Impact of Fe on the formation and aging of α-pinene secondary organic aerosol

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Key words: *Terpene oxidation, peroxides, particulate iron, Fenton chemistry, SOA formation & aging*

Abstract: Secondary organic aerosol (SOA) play a key role for air pollution, health and climate. They often comprise the majority of submicron particles by mass, and can become internally mixed with inorganic particles such as mineral dust. When transition metals like Fe are present, they can initiate aging processes that alter physical and chemical SOA properties. Furthermore, they can facilitate dissolution of minerals and form Fe-organic complexes, which are common in atmospheric particles. They can further generate reactive oxygen species within particles through dark peroxide and photochemical reactions (Fenton chemistry), leading to further aging of SOA by functionalization or fragmentation of organic species. Given the chemical complexity of SOA, a detailed understanding of these aerosol-aging processes and the subsequent impact they have on air quality, health and climate is lacking.

Here, we present data on the chemical composition of Fe-containing SOA and how it evolves over time. Particles were produced by forming SOA via α-pinene ozonolysis on both $(NH_4)_2SO_4$ or Fe-containing seed particles in an atmospheric simulation chamber under dark conditions at low and high relative humidities (RH). This allowed us to probe the impact of dark e.g., peroxide, reactions on aerosol aging with varying aerosol mixing states. Additionally, the impact of photochemically driven Fenton chemistry was studied by irradiating particles with UV light. Aerosol bulk composition was determined using extractive electrospray ionization mass spectrometry, allowing for high chemical and temporal identification of oxidation products, i.e., monomers and dimers. At low RH, all particles were found to contain a higher fraction of monomers, compared to dimers. In contrast, at high RH the monomer/dimer ratio was smaller when Fe was present due to rapid condensed-phase oligomerization reactions. This increased gas-particle partitioning of semi- and low-volatility species, increasing SOA mass. As Fe-containing SOA aged, the monomer/dimer ratio remained small; however, the composition shifted towards lower carbon number monomers and dimers likely from Fe-driven fragmentation reactions. This suggests that Fe-catalyzed reactions affect the composition of SOA, particularly at higher RH, as is common in many regions of the troposphere.

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TeraHertz spectroscopy for aerosols studies

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The Earth is undergoing climate change in which variations in the atmospheric environment play a crucial role. Knowing the interactions between radiation (solar and/or telluric) and matter suspended in the atmosphere (aerosols) is essential. It is essential to measure and interpret the spectral response of aerosols in the widest possible range.

The TeraHertz spectral domain is located between that of infrared and microwaves, long neglected due to lack of sufficiently sensitive detectors, sufficiently powerful sources and user-friendly measurement systems. Therefore, there are large gaps in the databases for complex refractive indices of atmospheric aerosols in the TeraHertz (THz) range. In order to respond to this problem, a measuring bench for aerosols was set up within the IEMN as part of the STEPSON project (TeraHertz spectrometer in time domain (THz-TDS) for the determination of the optical properties of micro and nano-particles suspended in a controlled environment (0.2 to 5 THz)). For the first time, an optical signal of desert dust constituent particles with sizes ranging from hundreds of nanometers to a few microns has been recorded in the THz range. The goal is then to exploit these experimental data in order to deduce the complex refractive indices. These sets of indices will be essential for interpreting the signals recorded by instruments on board a satellite platform (for example FORUM, which is scheduled to be launched in 2027) which will exploit the THz spectral range.

Atmospheric multiphase chemistry of organic species

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Key words: aerosol-cloud interactions, *atmospheric organic matter, water soluble organic compounds, aqueous phase processing, kinetics, deliquesced aerosol, water droplets*

Abstract:

Atmospheric organic matter has long been considered separately in the gas phase (VOCs), where it was considered highly reactive, and in the particulate phase, where it was considered non-reactive. This view was tremendously changed several years ago, and a more continuous pattern from reactive volatile, semi-volatile to low- and extremely-low-volatile species has been considered. The complexity was increased even more recently by the consideration of the presence of liquid water, and soluble organic species. Transport of reactive air masses to humid and/or wet areas is highly frequent in the atmosphere, making the study of deliquesced aerosols and aqueous phase processing particularly relevant.

Many studies have investigated the impact of liquid water on atmospheric (photo)chemical processes of organic species, and their results show the importance of such an approach to retrieve ambient observations. However, the complexity of such an approach induces high uncertainties, due to the necessity to investigate multiphase (photo)chemistry of polyfunctional organic compounds, and due to the lack of a detailed understanding of the chemistry occurring within the condensed phases. This presentation will give an overview of past and recent laboratory studies on bulk aqueous phase photochemical reactivity of organic species. From examples of polyfunctional organic compounds containing nitrates and/or (di)carbonyls, the presentation will focus on the fundamental differences of processes between aqueous and gas phase processes. The potential impacts of these processes will be discussed on the partitioning of organic compounds and their atmospheric lifetimes, on the oxidizing capacity, on the formation of secondary organic aerosol, and on their hygroscopic properties.

To further the atmospheric relevance of multiphase studies, the differences between aqueous droplets and bulk aqueous solutions will be discussed, and examples of integrated multiphase experiments of deliquescent aerosols in chamber studies will be presented.

Hidden Complexities of Chromophore Photochemistry in Aerosol Aging and Heterogeneous Nitrogen Oxide Chemistry

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Keywords: *Photosensitizer, Photochemistry, Multiphase, HONO, Nitrate*

Abstract: Highly oxidized natural organic matter contains photosensitizer moieties known to produce reactive oxygen species and directly mediate environmental reduction-oxidation chemistry. Photosensitizers are often discussed as reducing agents for NO_2 in the context of nitrous acid (HONO) sources, or as in situ oxidant sources able to enhance reactive uptake of volatile organic compounds and grow aerosol mass. This presentation will explore the exclusivity of this view by discussing examples where photosensitizers play a more complicated role in aerosol multiphase chemistry. I will show examples where photosensitizers mediate reactive oxygen and nitrogen levels in the condensed phase, leading to pathways that either enhance or decrease the yield of HONO formation from nitrate photolysis, depending on pH. In addition, we will show how reactive oxygen production arising from photosensitizers can decrease in aerosol mass, due to fragmentation and volatilization mechanisms. Results from aqueous phase, chamber experiments, and synchrotron radiation experiments will be presented to support these observations. We conclude that photosensitized chemistry regulates the mixed electrochemical potential of the environment and acts as both an oxidizing and reducing agent. This suggests that representation of photosensitizer chemistry in multiphase models requires knowledge of chromophore's role as both a source and sink of reactive oxygen and nitrogen in the aqueous phase.

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Excited triplet states from aerosol extracts competing with OH radical and singlet oxygen

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Key words: *triplet states, aerosol extracts, steady-state concentrations*

Abstract: Recently, excited triplet states of organic molecules ($^3C^*$) have been investigated for their abilities as oxidants in the aqueous aerosol phase. Here, we aim to understand if triplet states could have an influence on aqueous chemistry that is comparable to or even larger than two of the main oxidants in this environment, singlet oxygen ($^1O_2$) and hydroxyl radicals (•OH). Aerosols were collected in Grenoble, France both in winter and summer time during the period 02/12/2021 – 17/06/2022, and analyzed for their ability to produce $^3C^*$, $^1O_2$, and •OH. The optical properties of the aerosol samples show that compared to the summer samples, the winter samples have higher absorbance in the UV/Vis and likewise higher fluorescence intensity in the two major peaks in the excitation emission matrix (EEM), with $\lambda_{ex/em}$ = 225/415 nm and 320/425 nm. We estimated the steady-state concentration of these three oxidants in aerosols at sample concentrations of 10 mgC L^{-1}. The resulting concentrations of all oxidants were found to be larger in the winter samples than in summer samples. $[^3C^*]_{ss}$ showed an average of $(1.87 \pm 0.53) \cdot 10^{-13}$ M in winter samples, and $(9.95 \pm 2.9) \cdot 10^{-14}$ M in summer samples. $[^1O_2]_{ss}$ was found to have an average of $(6.51 \pm 0.32) \cdot 10^{-13}$ M in winter samples and $(4.40 \pm 0.28) \cdot 10^{-13}$ M in summer samples. For •OH the steady-state concentrations were $(2.01 \pm 0.52) \cdot 10^{-16}$ M in winter samples and $(1.07 \pm 0.30) \cdot 10^{-16}$ M in summer samples. These values give a trend of oxidant concentrations of $[^1O_2]_{ss} > [^3C^*]_{ss} > [\bullet OH]_{ss}$. Through a literature search for values of second-order rate constants between the mentioned oxidants with organic species in aqueous media, we observed a trend of $k_{OH,ORG} > k_{3C^*,ORG} > k_{1O2,ORG}$. Hereby, the triplet states appear to be highly important in aqueous media. By further experiments, the concentration of a single aerosol extract sample was varied (2.5 – 20 mgC L^{-1}), and we observed a plateau of $^3C^*$ concentrations at approximately $2 \cdot 10^{-13}$ M at 7.5 mgC L^{-1} (corresponding to $3 \cdot 10^{-5}$ µg PM / µg H_2O). From these observations, we suggest that in a range of similar particulate matter to water ratios (µg PM / µg $H_2O \approx (0.3 - 1) \cdot 10^{-4}$), this could serve as an estimate of steady-state triplet state concentrations in aerosols. Overall, this study emphasizes the relevance of excited triplet states compared to singlet oxygen and OH radicals in aqueous aerosols by including both estimated steady-state concentrations and literature second-order rate constants in aqueous solution for the oxidants with organic species.

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Spontaneous H_2O_2 formation at the interfaces of salt-containing aqueous droplets: A mechanistic study

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Key words: Air – water interface, Spontaneous chemistry, OH and H_2O_2 formation, Mechanistic investigation

Abstract: Sea-salt aerosol particles are considered to be a major source of biogenic atmospheric particles in marine environments. They play a key role in the atmosphere as they can affect cloud albedo and the Earth's radiation budget. Sea spray aerosols mainly consist of inorganic matter, but they can also contain organics in various mixing ratios. They represent a large fraction of interfaces in the atmosphere, since their size can range between sub-micron to super-micron, depending on their composition and the ageing processes. There is now much evidence that OH and H_2O_2 can be spontaneously formed at the air – water interface of aqueous droplets due to the presence of a strong electric field (~10^9 V m^{-1}). OH^- anion has been suggested that it partially exist as an ion pair ($OH^{\cdots}e^-$), which may undergo charge separation in the presence of this electric field. This can lead to OH radical and electron production, via $OH^- \rightleftharpoons OH^{\cdot} + e^-$, while H_2O_2 can be formed via subsequent reactions.

In this study, we investigated the interfacial production of H_2O_2 in salt-containing droplets. We performed measurements on droplets generated by the nebulization of Na_2SO_4, NaCl, NaBr and NaI bulk solutions, as their ions are the most in marine aerosols. We investigated how the presence of different halides in aerosols could influence the spontaneous H_2O_2 formation and also their potent involvement in the total mechanistic scheme. The effect of bulk concentration on H_2O_2 production was also explored. Furthermore, experiments at different bulk pH levels were also carried out, so as to assess the effect of the acidity/alkalinity on oxidants formation. Finally, to enhance our understanding in the reactions that participate in the H_2O_2 production, we performed a mechanistic investigation. The role of O_2 to the overall process was also examined.

All the experiments provide evidence that H_2O_2 is spontaneously formed at the air–water interface of salt-containing aqueous droplets. NaBr droplets, led to higher H_2O_2 production probably due to the ability of Br^- to generate solvated electrons and Br radicals in the presence of a strong electric field, like OH^-. O_2 was found to play a key role in the H_2O_2 production, as it shifts the equilibrium of the main reaction $OH^- \rightleftharpoons OH^{\cdot} + e^-$ to the right, promoting the OH and electrons formation. Our mechanistic investigation revealed that H_2O_2 formation involves different and complex reaction pathways that should be further examined via theoretical calculations. Results from this study are expected to significantly improve our insights on the interfacial processes that occur in atmospheric droplets and on the atmospheric multiphase oxidation chemistry.

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Molecular-scale view of the interaction of water and ice with organic species of atmospheric interest

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Key words: *Cryogenic technique; spectroscopy; molecular interactions; ice; water; organics*

Abstract:

The cryogenic techniques coupled to spectroscopies (FTIR, UV-visible, …) are powerful tools to study room temperature unstable species (reaction intermediates, unstable isomers, …). Molecules are trapped either in rare-gas matrix or on ice surface in controlled conditions. The low temperature and trapping conditions allow to explore molecular structures and interactions i.e. hydration process from complexes to aggregates and then to ice. Moreover, samples may be kept for long time period (over days) allowing multiple irradiation (selective or broad band) and heating cycles.

In this presentation, we will propose two examples of studies related to aerosol of atmospheric interest: the first on the hydration process of 3 methyl-1,2,3-butanetricarboxylic acid (MBTCA), a relevant tracer compound for monoterpene SOA formation and aging processes. The second will focus on the investigation of interactions between gaseous methyl iodine (from marine, vegetation or terrestrial sources) and various water ice surfaces, emphasizing the influence of trapping sites on the bonding and photofragmentation of CH_3I.

Acknowledgments

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Molecular cluster composition and aerosol formation over Siberian boreal forest.

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Key words: *new particle formation, molecular clusters, mass spectrometry, anthropogenic-biogenic interactions, boreal forest*

Abstract:

In boreal forests, aerosol particles frequently form via gas-to-particle conversion, known as new particle formation (NPF). Compared to other boreal sites at similar latitudes, NPF was reported to occur less often in the Siberian forest. However, factors controlling NPF in Siberia remained unknown. To address this, we conducted an intensive measurement campaign at the observatory Fonovaya in the West Siberian taiga deploying atmospheric pressure interface mass spectrometer (APi-TOF) and aerosol particle counters during spring 2020. We observed unexpectedly high NPF frequency (50%) during early spring. After mid-April, NPF occurred on about 15% of the days, in line with measurements from previous years. During the onset of NPF in early spring, we detected formation and subsequent growth of negatively-charged clusters containing sulfuric acid and ammonia. During that period, the air was affected by pollution transport from industrial regions to south and south-west of the site resulting in elevated SO_2 concentrations. In contrast, late spring NPF was characterized by molecular clusters containing sulfuric acid and oxygenated organics. During late spring, air masses from clean sector to the north were more frequent resulting in lower SO_2 concentrations. Together with higher air temperatures, less sulfuric acid caused a decrease in the NPF frequency and particle formation rates. Based on the magnitude of particle formation rates and abundance of biogenic organic oxidation products within clusters, we hypothesize that early photosynthetic recovery, caused by Siberian heatwave, explains frequent NPF during early spring. Temperatures 1-5 C above normal boosted biogenic emissions, which subsequently mixed into the polluted air masses enhancing molecular clustering and growth. Given the strong warming trend in the region, our results suggest that within 25–30 years, the monthly NPF frequency during early spring in the West Siberian taiga can reach 40-60%, as is currently observed at the European boreal sites.

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Oxidation of Ions at the Air-Water Interface: Towards a General Classification of Surface and Bulk Reaction Kinetics in Aerosol

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Key words: *Surface Chemistry; Air-Water Interface; Kinetic Modelling; Mass Spectrometry; Molecular Dynamics*

Abstract: Multiphase chemistry is ubiquitous in the environment and particularly relevant to atmospheric sciences, influencing aerosol formation, cloud properties, and trace-gas concentrations. Nevertheless, chemical and physical processes at gas-liquid interfaces remain obscure due to the often overlapping timescales of diffusion, surface-adsorption, reaction, and solvation. Here we present experimental and theoretical work investigating the oxidation of iodide ions by trace ozone at the air-water interface in single microdroplets, a system that is uniquely sensitive to the underlying transport phenomena across the interface. Reaction kinetics are obtained using single-microdroplet analysis with mass spectrometry while varying reactant concentrations to explore various limiting kinetic cases. We employ molecular dynamics simulations of the nano-scale interface to understand key kinetic processes such as O_3 desorption and solvation, and static properties such as the free energy profiles across the surface. Furthermore, we explore the potential role of spectator ions interfering with surface reactivity by altering the free-energy profile of the reactive species near the interface.

Combining our results from molecular simulations and experiments, we construct a general kinetic framework for multiphase reactivity benchmarked against a set of oxidation reactions of inorganic and organic species. This modeling approach attempts to identify key “kinetic regions” that characterize the microdroplet through a careful analysis of the timescales of gas and liquid-phase diffusion, gas-adsorption to the interface, solute diffusion and desolvation at the liquid surface, and chemical reaction between species. Specific focus is given to the chemically-active regions defined: the surface region on the scale of density attenuation from the liquid to the gas phase, the sub-surface region on the scale of the reaction-diffusion length of the impinging gas, and the aerosol interior on the scale of the particle radius. Analytic expressions for reactive uptake of a gas by a microdroplet are presented on the basis of this kinetic description. Ongoing work is discussed wherein the multiphase chemistry of a more general liquid-gas interaction can be classified on the basis of core chemical and physical properties such as reagent concentrations and surface propensities, diffusivities of solutes and solvent, and volumetric dimensions.

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Neural-Network-based Simulations of Acidity at the Surface of Aqueous Aerosols.

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Key words: Aqueous Aerosols, Acid-Base Chemistry, Machine Learning, Molecular Simulations, Vibrational Spectroscopy

Abstract: Understanding the acidity of aqueous aerosols is key for rationalizing many atmospherical processes. However, whether the air-water interface is more or less acidic than bulk water is a long-standing debate. While the negative value of the surface charge of water has been interpreted as a proof of the presence of excess basic hydroxide anions in the interface region, surface tension measurements and non-linear vibrational spectroscopies point to an increased presence of acidic hydronium cations [1,2]. Determining the thickness of the interfacial region that is being probed in different experiments and to what extent the acid-base properties are modified with respect to the bulk are some of the main difficulties in solving this disagreement [3]. Furthermore, a surface-induced change in acid-base properties implies a dependence of this key quantity on the system size, which can be critical for the smaller systems such as, *e.g.* nucleation aerosols.

We employed novel neural-network-based simulations to probe the acidity of the air-water interface with a molecular resolution. Our results unambiguously show that hydronium cations are favoured at the air-water interface with respect to hydroxide anions. This has unexpected consequences both for the acid-base reactivity of any air-water interface and for the pH of the smaller interfacial systems [4]. We have also employed a new methodology to compute Sum-Frequency Generation spectra of pure and acidified water surfaces, as this technique provides one of the main experimental evidences of interfacial excess protons. Our simulations reproduce all the qualitative features of the experimental spectra, which both validates our results concerning the surface activity of hydronium cations and provides a molecular interpretation for their spectral signature.

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Air pollution and health: Novel concepts for characterization of the toxicological impact and the organic composition of ambient aerosols and emissions

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Air pollution with inhalable particle matter (PM) is known to be one most severe environmental health-risks worldwide (WHO, 2001). The investigation of the adverse effect mechanisms of aerosols (i.e. suspended, airborne particles) and in particular the impact of the organic fraction is a complex, multidisciplinary task with many scientific and technological challenges. In order to better understand the causes of the health effects, new methods and technologies for a more comprehensive characterisation of the chemical composition and physical properties of aerosols (i.e., particles and gases) need to be developed. Furthermore, improved biological assessment approaches for the adverse toxic effects of aerosols are needed. New approaches for both, the organic chemical and the toxicological characterisation of aerosols are presented, discussed and demonstrated by application examples. In a first part, an improved methodology to directly assess the toxicological impact caused by aerosols is presented. In the last decade, air-liquid-interface (ALI) exposable biological lung models using human lung cell-cultures were established. With current automated exposure stations field studies at emission sites are possible. The ALI cell exposure approach therefore is with state-of-the-art biological effect analysis (e.g., transcriptomic analysis or functional assays). As an example, ALI studies elucidating the impact of atmospheric photochemical aging on aerosol health effects are presented. Fresh and photochemical aged emissions of e.g., ship engines, aircraft engines and cars (EURO 6 level) were tested, showing a significant toxification of the emissions by the photochemical aging for cars with different fuels. This highlights the important influence of atmospheric chemistry for the adverse health-outcome of emissions and air pollution. In the second part new aerosol analytical concepts for an improved characterization of the organic fraction of aerosols based on Photo Ionization Mass Spectrometry (PIMS) are briefly introduced. Photo Ionization (PI) is in particular well suited to address the pattern of the highly health relevant Polycyclic Aromatic Hydrocarbons (PAH) in PM for on-line analysis or continuous measurement settings. The PIMS approaches include an improved on-line Single Particle Mass Spectrometric (SPMS, Schade et al, Anal Chem. 2019) that allow the measurement of PAH profiles of individual single aerosol particles, giving new insight into the mixing state of air toxicants (PAH/metals/soot) and source contributions (ambient air). Another approach measures the PAH evolving from a PM-loaded filter punch during a thermal-optical carbon analysis (i.e., a EC/OC measurement). Finally, the desiderata for innovative aerosol and health research are discussed.

Beyond Oxidative Potential: Multiphase Kinetic Modelling of Aerosol Health Effects

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Key words: *Health, Multiphase Chemistry, Modelling, Oxidative Potential*

Abstract: The inhalation of atmospheric aerosols is correlated with enhanced morbidity and mortality, however, our molecular-level understanding of the interactions of aerosols and their constituents with the human body remains poor. Oxidative stress in the lung due to an excess presence of reactive oxygen species (ROS) is the leading hypothesis for the mechanism behind the adverse health effects of atmospheric particulate matter. Accordingly, measurements of the production of ROS by atmospheric particles in oxidative potential (OP) assays are an increasingly popular means to assess their toxicity. ROS, however, are already present and released in significant quantities in the human body.

We used a multiphase chemical kinetics model of the human respiratory tract, KM-SUB-LUNG, to quantify the effects of particulate pollutants on the production of ROS and oxidative damage in the epithelial lining fluid of the lungs. The model aims at connecting laboratory investigations of air pollutant properties with the epidemiological evidence for air pollution health effects by providing quantitative, physiological metrics for air pollution toxicity. Our findings challenge the paradigm of chemically-induced ROS production by particulate matter in the lungs, and hence their OP, as the determinant of their health effects. We find the total chemical ROS production of inhaled particles to be small in comparison to the various endogenous or even ambient gas phase sources of ROS[1], and the model cannot explain levels of oxidative stress markers through air pollutant-mediated chemistry[2]. We postulate that the adverse health effects of particles may arise from conversion of peroxides into more reactive species such as the hydroxyl radical[3] or are the result of a complex oxidative stress – inflammation feedback[4]. The analysis highlights remaining uncertainties in the relevant physical, chemical and biological parameters, suggesting a critical reassessment of current paradigms in elucidating and mitigating the health effects of different types of air pollutants.

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Aerosol Particle Drying, Deposition and Resuspension.

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Key words: *phase behaviour; evaporation and condensation; surface impaction; resuspension*

Abstract:

Studies of the microphysical processes occurring in aerosol at the single particle level can provide considerable insight into the mechanisms of aerosol transformation, transport and loss in the atmosphere and beyond. Moving beyond studies that examine isolated particles in a gas phase, we will report the development of new techniques to study particle-surface interactions, specifically the processes of droplet drying, subsequent deposition on a surface and then potential resuspension. Such a sequence of processes may be of considerable importance in, for example, the survival and transmission of airborne pathogens in the environment where viruses and bacteria are carried in drying respiratory droplets, deposit on surfaces in a state of partial dryness, and can then be resuspended in an airflow.

We will show that a falling droplet column (FDC) can be used to study the drying kinetics and phase behaviour of droplets with high reproducibility, allowing studies of, for example, the kinetics of liquid-liquid phase separation or the drying of droplets containing nanoparticles, including viruses. Using the FDC or a quadrupolar trap to prepare dry particles, particles can be deposited on surfaces in a regular array, at selected times and in states of known moisture content, and imaged by high frame rate imaging. Such an approach allows studies of surface impaction of picolitre droplets, considerably smaller than typical sessile drop measurements. Finally, the resuspension of these monodisperse particles with highly reproducible morphology into the gas phase can be studied in a miniature wind tunnel.

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Characterization of the Surface Layers of Organic Particles with Matrix Assisted Ionization in Vacuum-Mass Spectrometry (MAIV-MS) and a Little "Magic"

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Abstract

Aerosol particles are central to many atmospheric processes that affect human health, air quality, and climate. Understanding the gas-surface interactions that control particle growth, heterogeneous chemistry, and water uptake requires an understanding of the molecular surface composition of particles. Characterizing particle surface composition is challenging due to the small amounts of material relative to the bulk and to the difficulty in preserving molecular information. We present results using a mass spectrometry technique that provides molecular identification of particle surface layers in real time without the use of an external ionization source. The technique, Matrix Assisted Ionization in Vacuum (MAIV), uses solid dicarboxylic acid particles as a matrix compound that ejects ions from the surface as they evaporate upon entering the mass spectrometer inlet. The surface-sensitivity of MAIV is shown by coating the particles with thin layers of compounds ranging from small diacids to high molecular weight α-pinene ozonolysis products, which results in the detection of parent ions from approximately the top 15 nm of the particle. Additional studies of hydroxyl radical oxidation at the surface of solid glutaric and adipic diacid particles show that labile peroxides are formed with unexpectedly high signal intensities, and that the peroxide intensities are similar to those of the more stable carbonyl and alcohol products. The gentle ionization and faster analysis of this online technique facilitate the detection of peroxides that are subject to significant decomposition, as observed in more conventional, offline, bulk particle analysis. The combined results show that MAIV provides a unique mass spectrometry approach for examining particle surfaces during particle growth and heterogeneous chemistry. Insight into the MAIV ion generation mechanism will be discussed.

Keywords: surface, sensitive mass spectrometry, ionization, peroxides, organic particles

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[*] Speaker

Interaction of PAH-based species in the gas phase with ultraviolet radiation.

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Key words: polycyclic aromatic hydrocarbons; photoionisation; photofragmentation; photoelectrons; astrochemistry; laboratory astrophysics

Abstract:

In star forming regions, polycyclic aromatic hydrocarbons (PAHs) are strongly coupled to ultraviolet (UV) irradiation. This interaction leads to molecular processes that impact the physical and chemical conditions in these environments [1]. Key molecular parameters to be studied include UV photo-absorption cross-sections, ionisation yields, electron kinetic energy distributions and fragment branching ratios (BRs). A related objective is also to study the chemical composition and transformation of PAHs, taking into account the processes involved in energy relaxation and photochemical reactions.

We have combined several experimental techniques to study these processes and quantify the relevant parameters. We used ion traps to study the fragmentation of PAH cations, their alkyl derivatives [2] and the products of PAH reactivity with oxygen and water. Using tunable VUV light from the DESIRS beamline at SOLEIL, we were able to derive ionisation yields and the evolution of fragment BRs as a function of the energy of the VUV photon absorbed [3]. At DESIRS, we also used imaging photoelectron photoion coincidence spectroscopy to study the ionisation and dissociative ionisation properties of neutral PAHs and PAH clusters [4]. We have also started to carry out photoelectron spectroscopy on PAH nanoparticles.

I will summarize how these experiments are helping us to make progress in our understanding of the interaction of UV light with PAH-related species, and in assessing the impact of this interaction on the physical and chemical conditions in astrophysical environments, but also possibly in other environments, such as the atmospheres of planets, including the Earth.

References

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Transformations of biomass burning aerosol components and the effects on oxidative potential and cytotoxicity

Yinon Rudich, Chunlin Li, Zheng Fang, Mihcal Pardo - Weizmann Institute
Jianmin Chen – Fudan University
Xinming Wang – Guangzhou Institute of Geochemistry
Alexander Laskin, Diego Calderon-Arrieta – Purdue University

In recent decades, an increasing trend in wildfires has been observed in many parts of the world, coinciding with increased temperatures and drought severity. Apart from wildfires, wood, peat, and agricultural residues are frequently burned by humans. Several studies have indicated that exposure to biomass burning smoke is associated with all-cause and cardiovascular mortality and respiratory morbidity. This talk will focus on the daytime and nighttime atmospheric transformations of HULIS and phenol-containing aerosols, which are dominant components of biomass burning emissions. Specifically, we will focus on how the chemical transformations of the aerosols affect their oxidative potential, and their cytotoxicity.

The production of singlet oxygen from brown carbon cooking organic aerosols (BrCOA) under indoor lighting.

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Key words:
photochemistry, singlet oxygen, cooking aerosols, brown carbon

Abstract:

The first excited state of triplet state O_2 is singlet state $^1O_2$ and this oxidant is formed naturally in the environment, for example in sunlit waters from indirect photochemistry of dissolved organic matter. Our group has recently demonstrated that $^1O_2$ can be formed from brown carbon in the atmosphere, opening up questions about the sources, the sinks and the impact of aging of this particular oxidant. We propose that $^1O_2$ can be a competitive oxidant in the atmosphere. Thus far, our research has quantified $^1O_2$ in lab-generated brown carbon and in field-collected PM2.5.

Most recently, we identified sources of $^1O_2$ from cooking organic aerosols under indoor light conditions. We used an impinger to collect aerosols from a range of cooking dishes, including pancakes, pan roasted Brussels sprouts and vegetable stir-fries, and irradiated these samples in a photoreactor with UVA and fluorescent light bulbs as well as at a sunlit windowsill. Using furfuryl alcohol as a probe for $^1O_2$, we determined steady-state concentrations of $^1O_2$ using liquid chromatography and calculated $^1O_2$ quantum yields for each cooking aerosol sample. Our results show that under all indoor lighting conditions, brown carbon cooking organic aerosols (BrCOA) can indeed sensitize $^1O_2$. The variability of the steady state concentrations of $^1O_2$ was as large between dish type as between replicates of the same dish. This result suggests that $^1O_2$ production is not dish-type dependent, but rather produced across a range of BrCOA types. For example, in solutions of BrCOA of pancakes, roasted Brussels sprouts, and vegetable stir-fry under UVA light, the $^1O_2$ concentrations were 2.6e-13 M, 2.2e-13 M, and 3.1e-13 M, respectively. We then normalized these concentrations to the rate of absorbance to obtain quantum yields up to 6.1%. Both the quality and the quantity of the chromophoric BrCOA are important for predicting the quantum yield. The aim of this presentation will be to give an overview of how atmospheric $^1O_2$ impacts the oxidative capacity of the atmosphere.

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Where and how to study SOA formation and ageing at the molecular level and on the field?

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The aim of this presentation is to outline the selection criteria and characteristics required for a measurement site to investigate, in ambient air, the physico-chemical processes involved in the formation and ageing of secondary organic aerosols (SOA) at the molecular scale. Generally speaking, given (i) the extreme complexity of atmospheric reaction mixtures, (ii) the continuous variability of experimental conditions (temperature, relative humidity, concentrations of oxidizing species and air mass turbulence etc.) and (iii) the impossibility of repeating experiments by choosing the parameters to be varied, field studies at the molecular scale represent a real challenge to describe the chemical reactions at work in the atmosphere. Considering more specifically the multiphase processes (gaseous, gas-solid, gas-liquid, condensed phases) involved in the reactivity of SOA, the difficulties are even larger. Nevertheless, it seems essential, in order to ensure understanding these processes, to compare their description when studied in controlled and simplified environments such as reactors (flow or quasi-static) or atmospheric simulation chambers, with the measurements obtained in the real atmosphere.

These considerations, which are intended to be general, will be illustrated by the example of the LANDEX site located in the Landes forest in southwestern France. The Landes forest is a man managed-forest planted almost exclusively with maritime pines, resulting in specific high monoterpene (mostly α- and β-pinene) and very poor isoprene emissions. As it may also benefit from strong solar irradiation, sea spray inputs as well as air masses weakly impacted by anthropogenic emissions, the LANDEX site can be considered as an open-air laboratory to study biosphere-atmosphere interactions and more specifically biogenic SOA formation and fate at the molecular level. The relevance of this site to document scientific questions related to BSOA will be illustrated by some major results obtained over the last 10 years as well as some future outlooks.

Atmospheric Aerosol Chemistry: Climate and Air Quality

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INAR (Physics), University of Helsinki

Key words: aerosols, mass spectrometry, HOM, air quality

Abstract:

Despite much effort in the past decades, uncertainties in both climate impacts and health effects of atmospheric aerosols remain large. During the last 25 years, aerosol mass spectrometry (AMS) has shown that sub-micron aerosol chemical composition is roughly 50:50 inorganic and organic worldwide, with secondary highly oxidized organics dominating the latter. Parallel application of chemical ionization mass spectrometry (CIMS) has provided the first observation of molecular cluster ions involved in atmospheric nucleation, including detection of highly oxidized multifunctional (HOM) organics in the gas phase. These results will be discussed in the context of their impact on atmospheric aerosols, air quality and climate; from the boreal forest to Chinese megacities

Contribution of Particle Photooxidants to Winter Secondary Organic Aerosol Formation in a Subarctic City

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Key words: photooxidants; secondary organic aerosol; biomass burning; arctic; brown carbon

Abstract: Subarctic cities notoriously experience severe winter pollution episodes with $PM_{2.5}$ concentrations above 35 $\mu g/m^3$, the EPA's 24-hour standard. Biomass burning (BB) for residential heating is a major source of primary particles in winter, making the $PM_{2.5}$ rich in light-absorbing brown carbon and therefore prone to multiphase photochemistry. Typically, photochemistry is expected to be limited at high latitudes during winter due to large solar zenith angles and short daylight hours. However, we predict that despite the low photon flux, brown carbon in particles absorbs sunlight to produce abundant photooxidants, including triplet excited states of brown carbon, hydroxyl radical, and singlet molecular oxygen. These photooxidants then react with semi-volatile BB gases, such as phenols, to produce secondary organic aerosol (SOA). Here, we explore the role of particle photooxidants in SOA formation during winter pollution events in Fairbanks, Alaska. In the winter of 2021, as part of the ALPACA field campaign, we collected $PM_{2.5}$ filter samples, measured photooxidants produced by the $PM_{2.5}$ under laboratory conditions, used our measurements to model photooxidant production in concentrated aerosol liquid water, and then modeled gas and particle SOA formation in Fairbanks. We find that high brown carbon concentrations during pollution events led to abundant particle photooxidant production. We also predict that particle SOA formation was significantly faster than gas SOA formation, highlighting the unexpected potential role of particle photooxidants to $PM_{2.5}$ formation during pollution episodes in Fairbanks, Alaska.

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Mechanistic Insight into Radical Formation during the Photochemical Aging of Secondary Organic Aerosols

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Key words: *Photochemical Aging, Free Radicals, Secondary Organic Aerosol*

Abstract:

The photochemical aging of atmospheric aerosols alters its physical and chemical composition, which may have important implications on the toxicity and climate effects of these particles. Recent work has explored the impact of photochemical aging on particle composition, but there is limited understanding on the molecular-level processes occurring. This study applies electron paramagnetic resonance (EPR) spectroscopy with a spin trapping agent BMPO and high-resolution mass spectrometry (HRMS) to study the formation of reactive oxygen species (ROS) and free radicals during the irradiation of lab generated secondary organic aerosol (SOA). This work includes a summary of the radical formation in SOA derived from terpenes (α-pinene, α -terpineol, β-ocimene, isoprene), phenyl derivatives (phenol, styrene, toluene, guaiacylacetone) and furans (furan, furfural) to provide insight into the aging mechanisms for different classes of SOA precursors prominent in biomass burning emissions. EPR analysis reveals that terpene SOA produced the most radicals including $HO_2\cdot$, carbon centered organic radicals (R·), and oxygen centered organic radicals (RO·) followed by furans which also produced $HO_2\cdot$ and R· with less substantial contributions from RO·. Phenyl derivatives produced noticeably fewer free radicals consisting solely of $HO_2\cdot$ and R·. HRMS analysis was used to identify the organic radical adducts detected via EPR for α-pinene, furfural, and phenol SOA. These results identify radical intermediates produced during photolysis of SOA which provides potential insight into the mechanisms involved in the photochemical aging process.

Accelerated and unexpected in-particle chemistry

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Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland

Key words: Photochemistry, heterogeneous aerosol chemistry

Abstract:

Accelerated in-particle photochemistry

Photochemical processes have been identified as the main causes of degradation and oxidation of matter in atmospheric aerosol particles. When light interacts with an aerosol particle, the light intensity can be greatly amplified inside the particle as the latter acts as a light-amplifying cavity. These optical confinement effects result in an acceleration of photochemical reactions in aerosol particles compared with reactions in the extended condensed matter.

Unexpected in-particle chemistry

This part of the talk will address specific examples of unexpected chemical reactions in particles which were recently observed in our laboratory. A final understanding of the causes and the involved mechanisms behind the observed processes is still missing. Nevertheless, we suggest preliminary explanations that are in agreement with the observed phenomena.

PLEASE NOTE : 1 page maximum

Determination of the viscosity and surface tension of levitated droplets at supercooled temperatures

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Key words: *(viscosity, surface tension, supercooled, levitated)*

Abstract

The physical, chemical and optical properties of atmospheric aerosols dictate their contribution to the Earth's radiative balance. In order to further understand the impact of aerosols on the climate, it is therefore necessary to measure their properties. Two important physical properties of aerosol are viscosity and surface tension. Viscosity plays a key role in multiple aerosol processes, impacting reaction rates and atmospheric lifetime, as well as influencing the ability of organic aerosol to act as ice nucleating particles. Furthermore, diffusion of reactant molecules within the aerosol bulk phase is influenced by viscosity which in turn impacts aerosol chemical composition and optical properties. Surface tension of atmospheric aerosol is a key property because it is closely linked to cloud droplet activation.

Here we report a new method[1] to determine the viscosity and surface tension of levitated droplets under atmospherically relevant conditions of temperature and humidity. The method is important because it is currently the only non-contact method capable of probing these properties at supercooled temperatures relevant to aerosol and cloud droplets at different heights in the atmosphere. Furthermore, it utilises small sample volumes providing the potential to measure real atmospheric samples and also allows the study of aerosol processing in real time. Another advantage of the method is that viscosity and surface tension are determined from the same experiment using one analysis method. Here I will present proof of concept measurements for water droplets, and dilute sucrose solution droplets at supercooled temperatures. I will also present preliminary data for water-soluble wood smoke aerosol and discuss applicability of the method.

The method represents a breakthrough for the atmospheric chemistry community where viscosity and surface tension data are typically only available at ambient conditions. Results of the low temperature measurements will provide added insight into a range of aerosol processes e.g., the effect of viscosity on the rate of atmospheric ageing. The method can be used towards a detailed molecular understanding of atmospheric aerosol processing when used in conjunction with other analytical techniques.

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Chemistry in nanometer aerosol particles: Flow tube experiments with Diels-Alder reactions as a model system

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Key words: reactive uptake; particle growth; aerosol chemistry; nucleation

Abstract:

There exist a number of physicochemical arguments to assume that chemical reactions take place differently in nanometer particles than in larger aerosol particles. One of these differences is the Laplace pressure in very small particles, which is caused by the surface tension of the interface between the particle and the gas phase. The Diels-Alder reaction, a well-studied addition reaction in organic chemistry in which a diene reacts with an activated alkene (the dienophile), is known to be a pressure-dependent reaction and is used here as a model system. It is known from this reaction that higher pressure promotes the bond-forming reaction. This system therefore offers the possibility of investigating a pressure-sensitive chemical system in nanometer-sized aerosol particles. By selecting a suitable dienophile in the particle phase and dienes in the gas phase on the basis of reactivity, volatility and detectability, the growth of the particles was observed to determine whether a reaction has taken place and whether it proceeds at different rates in particles of different sizes. The corresponding growth factors for monodisperse 30-, 60- and 90-nm aerosol particles from two reaction systems were determined. The particle size determination was carried out using a scanning mobility particle sizer (SMPS) and the characterization of the reaction products by thermal desorption coupled with a gas chromatography-mass spectrometry system (TD-GC-MS).

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Sea-salt hygroscopicity and crystallization of their mixture with oxalic acid.

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Key words: *Sea-salt, phase transition, sea-spray, single particle, hygroscopicity.*

Abstract: Seas and oceans are producing a large fraction of the atmospheric aerosols. These aerosols are usually composed of a mixture of inorganic salts, organic and biogenic matter. Particles made purely from the inorganic salts are usually called sea-salt particles, while they are called sea-spray when organic or biogenic matter are also present inside the particles. Sea-salt and sea-spray particles are playing a key role in numerous atmospheric processes such as cloud formation, hygroscopicity and phase transitions. Nonetheless, it remains unclear how these processes depend on the composition of the sea-salt or sea-spray particles.

In this contribution, we measured the hygroscopicity of single sea-salt particles isolated in air with an optical trap[1]. Single particle measurements allow to avoid ensemble averaging and hence permit to investigate processes which are otherwise difficult to observe. In addition, it is important to study aerosol particles isolated in air because they often experience different processes than deposited particles and bulk solutions. During this study, a multi-step phase transition was observed when a realistic sea-salt composition was used while simpler inorganic proxies such as sodium chloride showed no such behaviour[1].

A mixture of sea-salts with oxalic acid is also studied as a proxy for sea-spray particles. In this case, crystallization of the single particles was observed. The formed solid phase in the particle is most likely mono-sodium oxalate. If ions at low concentration, such as magnesium ions, are removed from the inorganic salts, the kinetics of such crystallization appear to be strongly influenced. These measurements highlight the importance of using realistic salt compositions to fully describe the complexity of atmospheric transformation experienced by sea-salt and sea-spray particles.

Reference

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Investigation of the Spontaneous Formation of Molecular Iodine at the Air/Water Interface with Optical Tweezers

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Key words: *optical tweezers, iodine, halogens, air/water interface, aerosols*

Abstract: Optical trapping has been a fast-advancing technology in the last decades, since its first demonstration by Arthur Ashkin in 1970. With the idea of using tight-focused laser light to trap and manipulate suspended particles, several applications in various fields have been explored, from biology to quantum physics, including aerosol particles. In this work, we modified a commercially available aerosol optical tweezers (Biral AOT-100 [1]) to study the activation of halogenated radicals in aerosol droplets, which is a key process in tropospheric chemistry [2]. The size of the droplets spans from few to tens micrometers, mimicking the behavior of fogs and clouds, but studying the phenomenon at the scale of the single particle, exploiting the exceptional sensitivity and time resolution of optical tweezers, as well as the stability over a long period of time. A part of the radiation used for the trapping is scattered by the particle, and can be used to provide physical and chemical characterization. More in detail, the physical information of size and refractive index can be achieved observing the known as whispering gallery modes of the Cavity Enhanced Raman scattering, that gives high-intensity sharp peaks in the 3200-3400 cm^{-1} range (asymmetric and symmetric OH-stretch of water respectively). The presence of sodium iodide in the trapped droplet, together with the charge separation due the intrinsic electric field at the interface of the droplet, leads to the spontaneous formation of I^{-} radicals, that in the presence of oxygen recombines forming molecular iodine [3]. The latter can be monitored over time with Resonance Raman spectroscopy, observing the rise of the Raman overtones of I_2 in function of time. This spontaneous effect can be studied in function of different parameters, such size, salt concentration and relative humidity.

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Investigating the Dynamic Surface Composition of Aerosol Droplets

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Key words: laboratory measurements, surface tension, surface composition, surfactant dynamics, kinetic model

Abstract: Due to the relatively large surface area compared to the volume of aerosol droplets, their surfaces become an important factor governing chemical and physical processes. For example, the unique chemical environment at the droplet-air interface has been invoked to explain enhanced reaction pathways observed in microdroplets. Additionally, the large surface area relative to bulk can affect the bulk concentration of surface-active molecules, as a significant proportion of these molecules will partition to the interface, leaving the bulk concentration depleted. While a few methods have been reported that can measure the surface properties and surface tension (which is directly related to surface composition) of aerosol droplets at equilibrium, techniques that are able to monitor the dynamic surface composition remain elusive. Yet, it is necessary to understand the dynamic properties of aerosol surfaces since these surfaces are constantly changing due to hygroscopic growth and interfacial chemical reactions.

This talk will describe a method of measuring the dynamic surface tension of droplets in the tens of picolitre volume range, microseconds after droplet formation, using a stroboscopic imaging approach. We find that the time-dependent surfactant partitioning is unique to different surfactants, even those with similar equilibrium surface tension properties (e.g., concentration dependent equilibrium surface tension and critical micelle concentrations). We use a kinetic model built in Kinetiscope to interpret these results, finding good agreement between the model and experimental results at a range of surfactant concentrations. We demonstrate that it can take many milliseconds for surfaces of these droplets to reach their equilibrium surface concentrations. These timescales are similar to, or even longer than, the reaction timescales observed during accelerated chemistry, and should be considered when attempting to explain observations of accelerated chemistry in microcompartments.

Accelerated Keto-Enol Tautomerization of Aqueous Malonic Acid in Micron-Sized Oil Emulsions

Brandon J. Wallace[a,b*], **Ashok Ajoy**[a,b], **Kevin R. Wilson**[b],

[a] Department of Chemistry, University of California, Berkeley
[b] Chemical Sciences Division, Lawrence Berkeley National Laboratory

Key words: chemical kinetics; reaction acceleration; optical trapping; Raman spectroscopy;

Abstract: In recent years it has been shown that microcompartments, such as aerosol particles, can act as efficient vessels for chemical reactions. In certain cases, reactions have been shown to occur more favorably in aerosol particles relative to the bulk, with orders of magnitude reaction acceleration being reported. While many mechanistic questions still remain regarding the fundamental driving forces of these accelerated kinetics, the interface has been shown to contribute significantly. To improve our understanding of chemical reactions in microcompartments, and the role of the interface, we have designed a novel microfluidic optical trap. As opposed to the often-studied air-water interface, currently less is known about the oil-water interface. With this technique, reaction kinetics of single micron-sized aqueous droplets in oil emulsions can be studied. We apply this methodology to investigate the kinetics of keto-enol tautomerization of aqueous malonic acid (MA). Using Raman spectroscopy of the trapped droplets, keto-enol kinetics can be quantified through deuterium-hydrogen isotopic exchange. We observe accelerated reaction kinetics, with as high as a factor of 2 acceleration compared to the bulk. We demonstrate the influence of size and concentration on the acceleration factor and compare these results to experiments on levitated aerosol particles to elucidate how different interfaces can influence chemistry.

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Accelerated Keto-Enol Tautomerization of Aqueous Malonic Acid in Micron-Sized Oil Emulsions

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[a] Department of Chemistry, University of California, Berkeley
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Peroxy radical recombination leads to an unexpectedly complex mixture of low-volatility products

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Key words: peroxy radicals, atmospheric chemistry, aerosol precursors, reaction mechanisms

Abstract: The least volatile organic compounds participating in atmospheric new-particle formation are very likely accretion products from self- and cross-reactions of peroxy radicals (RO_2). The mechanism of this reaction is remarkably complex. The first step is the recombination of the radicals on the singlet surface, forming a tetroxide (RO_4R') intermediate. The overall RO_2 + $R'O_2$ reaction rate is controlled by this step, and can be modelled either by standard reaction kinetic approaches (for systems where the step involves a substantial barrier), or by even simpler classical unreactive molecular dynamics (for cases with low or non-existent barriers).

The tetroxide subsequently dissociates into a ground-state (triplet) oxygen molecule ($^3O_2$), and two alkoxy radicals (RO + R'O), which must also be coupled as a triplet. While O_2…RO reactions may occur especially in smaller systems, the predominant fate of the three dissociation products is in most cases likely the escape of the $^3O_2$ molecule, and the transient formation of another intermediate: a ^{3}(RO…R'O) cluster. This cluster may then also dissociate, giving free alkoxy radical products (the main channel for most small RO_2), or undergo an alkoxy-alkoxy hydrogen shift to give alcohol and carbonyl products (the main channel for *e.g.* CH_3O_2 + CH_3O_2).

Our quantum chemical modelling indicates that for sufficiently complex RO_2 + $R'O_2$, the alcohol + carbonyl channel and especially the radical channel become uncompetitive. The ^{3}(RO…R'O) intermediates will instead undergo either direct intersystem crossings (ISC) to the singlet surface, or intramolecular scission or H-shift reactions inside one (or both) of the two alkoxy radicals, possibly also followed by an ISC. In both cases, subsequent recombination of the radical products gives rise to a complex mixture of accretion products, including not only ROOR' peroxides, but also ROR' esters, ethers and even RR' alkyl products with new C-C bonds.

We have carried out a qualitative analysis of the likely product distributions of these reaction channels for a variety of atmospherically relevant precursor molecules, such as monoterpenes. The coupling of peroxy and alkoxy radical chemistry described above gives rise to an explosive increase in chemical complexity: several hundreds of thousands of different accretion products, with widely variable volatilities and other properties, can be formed from just a handful of hydrocarbons and oxidants. Many of these products are structural isomers of each other, and thus indistinguishable for example in typical mass spectrometric measurements. In particular, many compounds previously identified as ROOR' peroxides may in fact be ethers or esters – which are likely even more efficient at promoting aerosol formation and growth due to their higher thermal stability. Another, more surprising finding was that as the complexity of the reactants (specifically, the number of -OOH and -ONO_2 groups) grows, so does the likelihood of ^{3}(RO…R'O) reaction channels eliminating a small inorganic radical, such as OH or NO_2, and thus inhibiting recombination to larger accretion products. This implies, for example, that systems undergoing rapid and extensive autoxidation (creating multiple OOH groups) may not be particularly efficient at forming extremely low-volatility accretion products.

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Generation of High-level Oxygenated Organic Molecule Data

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Key words: *extremely low volatile organic compounds; molecular data; machine learning; oxygenated organic compounds*

Abstract: The growth of secondary organic aerosols (SOA) in the atmosphere is driven by the gas to particle conversion of oxygenated organic molecules (OOM), which are products of rapid, successive oxidation of organic anthropogenic and vegetation emissions. The affinity of an OOM to the condensed phase is measured with its saturation vapor pressure (p_{Sat}). OOM with especially low p_{Sat}, e.g., a subclass called extremely low volatile organic compounds (ELVOC), are thus of particular interest in studying the formation of SOA.

Identifying OOM, and particularly ELVOC and their chemical structures is both experimentally and theoretically challenging: Measuring the very low p_{Sat} of ELVOCs is extremely difficult, and computing p_{Sat} for these often large molecules is computationally costly. In this work, we tackled the computational challenges to generate a high-level dataset of OOM, which allowed us to train machine learning models capable of predicting OOM p_{Sat}. Then, we employed these models for a targeted search for ELVOC in a pool of OOM.

This study was based on a pool of 157k OOM SMILES strings, generated via the simulated atmospheric oxidation of α-pinene, decane and toluene with the chemical mechanism generator GECKO-A (Aumont et al., 2005). For the calculation of a p_{Sat}, we first conducted a conformer sampling procedure with the COSMO*conf* program, followed by the actual p_{Sat} computation with the COSMO*therm* program. We designed a high-throughput computation workflow that allowed us to obtain the p_{Sat} of 31,637 randomly selected OOM, which we published, together with more than 7.2M conformer structures, in the *GeckoQ* dataset (Besel et al., 2023).

ELVOC are underrepresented in available datasets of atmospheric organic species generated with GECKO-A, because GECKO-A truncates the molecule generation. Thus, the value of statistical models built on such data are mitigated. We utilize an active learning (AL) approach to efficiently identify ELVOCs in a data pool of atmospheric organic species with initially unknown p_{Sat}. We assess the performance of our AL approach by comparing it to traditional machine learning regression methods, as well as ELVOC classification based on molecular properties. AL proves to be a highly efficient method for ELVOC identification with some limitations on the scope of ELVOC it can identify.

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Besel, V., Todorović, M., Kurtén, T. Rinke P., and Vehkamäki H. (2023), *Sci Data,* **10**, 450.

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In silico studies of the atmospheric reactivity of organic contaminants

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Key words: organic contaminants; atmospheric degradation; kinetics; reaction mechanisms; molecular simulations

Abstract:

The presence of atmospheric contaminants results either from direct emission from point sources: incineration, use of fossil fuels, industrial activities, etc., or from diffuse emissions or re-emissions from contaminated soils or waterbodies. This phenomenon concerns a great diversity of molecules, which originate in human uses or activities releasing volatile organic compound, containing a variety of different heteroatoms constituting a large category of emerging contaminants (pesticides, plastics, tire wear additives, PFAS, etc.). For many of them, the atmospheric pathway is their main mode of dispersion.

The primary route for the removal of contaminants from the atmosphere is by dry or wet deposition techniques. The chemical reaction initiated by major atmospheric oxidants (OH, O_3) are responsible for their transformation in the atmosphere. The products formed from these reactions may be hazardous and may lead to several negative implications. Deposited atmospheric fluxes of contaminants and corresponding degradation products also constitute an ecological risk for marine or terrestrial hydrosystems, apart from the potential human health risk induced by their presence in ambient air.

In this talk, we will provide insights in a better understanding of the atmospheric degradation for some of the compounds we are working on using modelling tools.

Water Plays Multifunctional Roles in Formation of Secondary Organic Aerosols in Ozonolysis of Monoterpenes: A Combined VUV Photoelectron Spectroscopy, Mass Spectrometry and DFT Study

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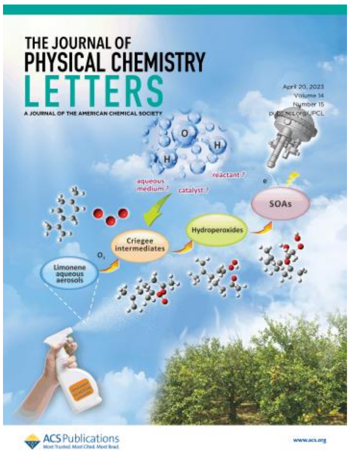
Key words: Ozonolysis, Monoterpens, Secondary organic aerosols, VUV photoelectron spectroscopy, Water, Criegee intermediates, High resolution mass spectrometry

Abstract:



"Atmospheric aerosol loading" is one of the nine major aspects that can affect the stability of Earth due to anthropogenic activities, according to the planetary boundaries theory[1]. However, the physic-chemical properties of aerosols from various sources, the key factors affecting their formation and transformation, and their impacts on Earth's stability, climate and sustainability remains to be better quantified and understood. Ozonolysis of monoterpenes represent one of the most important sources of SOAs. Although it is known that water may affect the aqueous aerosol chemistry, however, how it intervenes the formation of monoterpene-derived secondary organic aerosols (SOAs) at the molecular level remains unclear. Recently, we interrogate the valence electronic properties, chemical composition, and energetics of SOAs derived from monoterpene ozonolysis by combining synchrotron radiation-based aerosol VUV photoelectron spectroscopy, high resolution mass spectrometry, and DFT Study[2,3]. A special interest is focused on clarifying the roles of water in intervening in the formation of SOAs derived from monoterpene ozonolysis and their accompanying physicochemical properties. The ionization energies and valence electronic structures of three most important monoterpene aerosols, including limonene, pinene and pinene, have been measured for the first time. Combining with density functional theory (DFT) calculation and mass spectrometry measurements, we show that water, particularly water dimer, enhances the formation of SOAs via altering the ozonolysis energetics and pathways by intervening in its Criegee Chemistry, acting both as a catalyst and a reactant. The chemical composition of SOAs is also altered when water is present, as unraveled from high-resolution LC-ESI mass spectrometric measurements. The atmospheric implication will also be discussed.

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Reaction of Maleic Acid with Ozone at the Aqueous Interface

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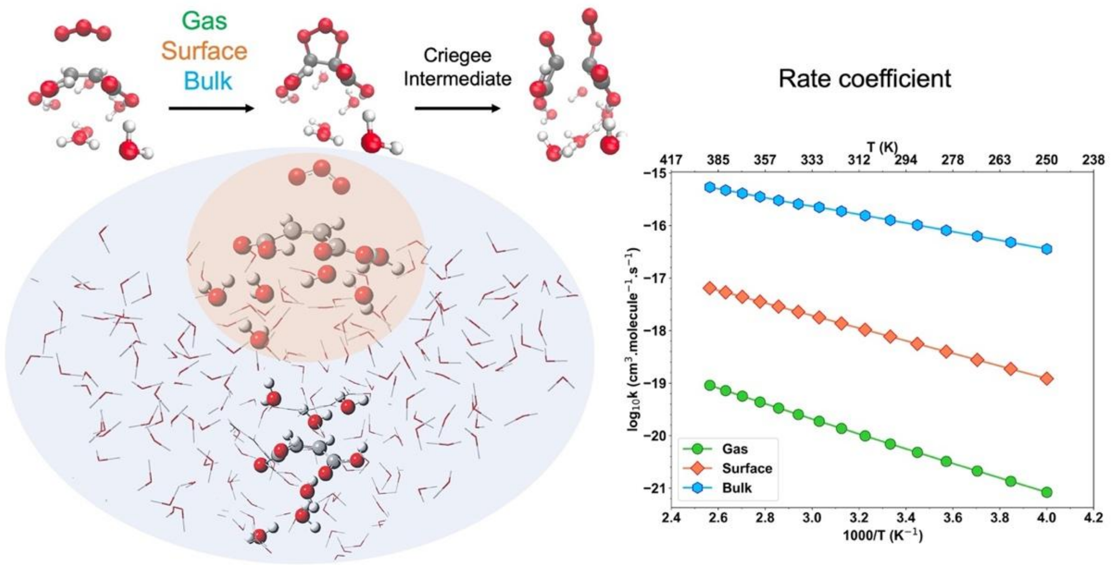
Key words: Secondary organic aerosols, Multiphase reactions, Criegee Intermediate, Rate Coefficient.

Abstract: The ozonolysis of unsaturated hydrocarbons holds significant importance for the atmosphere because it results in the generation of diverse oxygen-containing compounds like aldehydes, ketones, and carboxylic acids. The resulting Criegee intermediates (CIs) contribute to the creation of secondary organic aerosols (SOAs) through subsequent reactions with trace chemicals. Herein, we have investigated the multiphase ozonolysis reaction in a water droplet containing maleic acid (MA) using classical and quantum theoretical methods (QM/QM'). The relative occurrence of interfacial and bulk reactions is dependent on the bulk affinity of O_3 and the interfacial affinity of reacting MA, which is predominantly found in the bulk phase. Then, the kinetics of the initial step in different environments leading to the formation of the primary ozonide compound (POZ) have been evaluated. The results [1] reveal that the presence of water molecules enhances the initial reaction step compared to the gas phase, with a significantly larger rate coefficient in the bulk phase than at the interface. Furthermore, Ab Initio Molecular Dynamics simulations were employed to delve into the formation of the POZ and its subsequent breaking into CIs within a water cluster. The current approach provides insights into how the environment influences the complex kinetics and dynamics of these reactions.

Ref: [1] R. AbouHaidar, D. Duflot & C. Toubin (2023) Aerosol Science and Technology, 2023.
DOI: 10.1080/02786826.2023.2286341



Gas-phase kinetics of Criegee intermediate reactions with implications for aerosol formation in the atmosphere

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Abstract

Ozonolysis, wherein alkenes undergo 1,3-cyloaddition by ozone, produces a varied array of carbonyl oxides, commonly known as Criegee intermediates (CIs). These CIs are reactive species that can insert into labile hydrogenous bonds, such as those present in organic acids, alcohols, amines, sulphides and even water. Such insertion reactions lead to adducts that possess an increased mass and a concomitant reduced volatility, which may help explain the special capacity of ozonolysis reactions to produce secondary organic aerosol. Indeed, certain combinations of larger CIs and organic acids could lead to adducts of extremely low volatility and could therefore help initiate new particle formation. In some cases, such as that of the simplest CI, CH2OO, reaction with water vapour is expected to dominate the reactive flux. For some larger CIs, this reaction becomes slower, leading to longer lifetimes in the atmosphere, and an increased probability of insertion into other organic molecules.

Despite the importance of this chemistry, there is still a lot that remains unknown about the kinetics of these reactions. This is partly because of the limitations of current absolute kinetic methods, which rely on *gem*-diiodoalkane CI precursors, which are for the most part commercially unavailable, and possess low vapour pressures. A second consideration is that current absolute kinetic methods require a large excess of organic co-reactant. Both of these factors act together to limit the size and volatility of reactants that can be studied. For this reason, a new approach will be adopted. This will involve the development of a relative rate methodology in which the chemical reactivity of Criegee intermediates will be measured against a variety of organic co-reactants. The Criegee intermediates will be generated from *in-situ* ozonolysis reactions in large chamber facilities such as HELIOS (CNRS-Orléans). Since many ozonolysis reactions can produce several Criegee intermediates simultaneously, especially symmetric alkene precursors will be selected such that individual kinetic parameters can be determined unambiguously. Also, the chemical behaviour of some of the peroxidic products will be studied, using high-resolution PTR-MS, which will provide fresh insights into these remarkable chemical mechanisms.

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*Speaker

Multiphase Oxidation Chemistry in Indoor and Wildfire-impacted Environments

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Key words: *multiphase chemistry, oxidation chemistry, indoors, wildfires, autoxidation*

Abstract: Deciphering the mechanisms by which pollutants are chemically transformed into a variety of products is important for establishing our chemical exposure. In indoor environments, where we spend most of our time, such chemistry occurs readily on a variety of surfaces via pollutants arising from cooking, cleaning, and the use of commercial products. Most of the chemistry is driven by oxidation reactions, involving primarily ozone but also hypochlorous acid and the hydroxyl and nitrate radicals in some cases. An interesting question is the degree to which autoxidation processes occur indoors. Experiments will be presented for detailed reaction kinetics and mechanism studies, conducted under both lab conditions and in the real environment. The last part of the talk will discuss how the indoor environment can act as a source of pollutants to the outdoor environment, and that outdoor air can impact indoor spaces as occurs when wildfire smoke comes indoors. Such multiphase chemistry involving wildfire smoke, with a variety of oxidants, is likely relevant to both indoor and outdoor settings.

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Properties of secondary organic aerosol from oxidation of monoterpenes at different temperatures

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Key words: Biogenic secondary organic aerosol, phase state, chemical composition.

Abstract:

In this work we have studied the formation and properties of secondary organic aerosol from oxidation of two common biogenic volatile organic compounds, namely α-pinene and Δ^3- carene under different conditions of temperature and relative humidity.

Experiments were performed in the AURA atmospheric simulation chamber (Kristensent et al. 2017) at temperatures ranging from -16 to 20°C under atmospheric pressure. α-pinene and Δ^3- carene or mixtures of the two were oxidized in the dark by O_3. Particle size distributions were measured using a scanning mobility particle sizer and chemical composition of the particles was probed using a high-resolution time-of-flight aerosol mass spectrometer and off-line methods including UHPLC-QTOF-MS. Particle viscosity was probed based on a new technique which measures the restructuring of aspherical particles using a printed optical particle spectrometer (POPS) (Mahant et al. 2023).

The presentation will include a discussion of the physico-chemical properties of SOA particles formed under different conditions and the influence of temperature during SOA formation on these properties.

Acknowledgements :

We acknowledge the Danish National Research Foundation (DNRF172) through the Center of Excellence for Chemistry of Clouds, ACTRIS-DK, (5072-00032B), Independent Research Fund Denmark (0136-00345B, 8021-00355B), and the Aarhus University Research Foundation (AUFF-E-2021-6-26) for support.

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Limits of the molecular tracer approach in the understanding of SOA formation and fate processes

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Key words: BSOA, tracers, heterogeneous reactivity

Secondary organic aerosols (SOAs) have been the subject of all attention for several years. In this context, the LANDes EXperiment project (LANDEX) focused on the study of biosphere-atmosphere interactions at Salles-Bilos in the Landes forest ecosystem, in southwestern France. The aim of this long-term project was to study the formation and fate of biogenic secondary organic aerosols (BSOAs). In this work, the chemical composition of atmospheric particles was investigated using liquid chromatography coupled with time-of-flight mass spectrometry (LC-QTOF/MS) to achieve a molecular speciation of major BSOA markers. Their concentrations were determined in the $PM_{2.5}$ and PM_1 fractions for day- and nighttime periods along with the on-line measurements of VOCs (mainly terpenoids), either directly emitted by vegetation or generated through first or second generation oxidation steps (*e.g.* pinonaldehyde and nopinone). The complexity of the chemical composition of SOAs, the difficulty to characterize and evaluate their sources and subsequent aging processes, combined with the importance of SOAs in terms of impacts, make the need to use reliable atmospheric markers. During air mass transport, markers may undergo (photo-)chemical degradation in either gas or liquid phase but also heterogeneous oxidation (*e.g.* levoglucosan [1]). These last processes have been poorly documented for BSOA markers. Therefore, gas-surface reactions of 5 particulate-products arising from the atmospheric oxidation of α- and β-pinene (*i.e.* terebic acid, terpenylic acid, pinonic acid, pinic acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)) with the main atmospheric oxidants (OH, O_3) were investigated using a discharge fast flow tube. Methodologies and first results will be presented and discussed in the framework of the Landes forest.

References: [1] Hennigan et al. (2011), *Atmospheric Chemistry and Physics*, 11, 7669–7686.

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Particle-Phase Accretion Forms Dimer Esters in Pinene Secondary Organic Aerosol

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Key words: *Pinene, SOA, accretion, dimer*

Abstract: Secondary organic aerosol (SOA) is ubiquitous in the atmosphere and plays a pivotal role in climate, air quality, and health. The production of low-volatility dimeric compounds through accretion reactions is a key aspect of SOA formation. However, despite extensive study, the structures and thus the formation mechanisms of dimers in SOA remain largely uncharacterized. In this work, we elucidate the structures of several major dimer esters in SOA from ozonolysis of α-pinene and β-pinene—substantial global SOA sources—through independent synthesis of authentic standards. We show that these dimer esters are formed in the particle phase and propose a mechanism of nucleophilic addition of alcohols to a cyclic acylperoxyhemiacetal. This chemistry likely represents a general pathway to dimeric compounds in ambient SOA.

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Molecular composition of secondary organic aerosol using chromatography and mass spectrometry

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Keywords: chemical composition, secondary organic aerosol.
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Organic aerosol (OA) plays an important role in atmospheric chemistry, climate change and public health. While OA particles can be directly emitted into the atmosphere, they can also be introduced in the atmosphere by secondary organic aerosol (SOA) formation. However, our current knowledge of oxidation pathways and chemical composition of SOA is limited and poorly understood considering the difficulty of the chemical transport model to predict the OA mass in the atmosphere. It results in large uncertainties in the estimation of the impact on climate and air quality of atmospheric aerosols.

A better understanding of the SOA formation processes is essential to more precisely assess the health and environmental impacts of atmospheric particles. Analyzing the particle phase at the molecular scale of organic aerosol, which represents approximately half of the mass of fine particles (PM2.5) in the troposphere, constitutes a considerable analytical challenge. This is an essential necessity, both to elucidate their transformation mechanisms in the environment and to identify markers linked to the various sources and processes. Additionally, analysis of the particle phase at the molecular scale also makes it possible to complement and enrich the data obtained by analyzing the chemical composition of the aerosol as a whole (for example, via aerosol mass spectrometry (AMS)).

In this context, different chamber experiments and field campaigns will be performed to better understand the SOA formation and aging in the atmosphere. In CESAM chamber at LISA, a national facility of CNRS INSU, under various and controlled environmental conditions, different SOA formation from oxidation of individual anthropogenic precursors such as long chain alkanes, mono-aromatic or PAH or their mixing will be studied. Aside aerosol mass production, the mechanism was also investigated by measuring SOA composition after sampling on filter. Furthermore, during the ACROSS (Atmospheric Chemistry Of the Suburban forest) campaign from mid-June to the end of July 2022, to definitively improve the understanding of the impacts of mixing urban and biogenic air masses on the oxidation of atmospheric VOCs, filters were collected in the urban and peri-urban area (Rambouillet forest) of Paris.

The chemical characterization of secondary organic aerosols is an analytical challenge due to their complexity and their wide range of functionality, solubility and polarity, and low concentrations, down to trace levels. To address this complexity, different analytical technics will be used with the capability of detecting low and high molecular weight species (i.e., oligomers and long-chain highly functionalized compounds) by a combination of supercritical fluid extraction gas chromatography mass spectrometry (SFE-GC-MS), ultrahigh performance liquid chromatography coupled with ion-mobility (IMS) quadrupole-time-of-flight (QTOF) mass spectrometry (UPLC-TOF-MS) and ESI-UHR-MS (orbitrap) analysis.This coupling from the "regional platform for multi-media analysis of micro-contaminants" (PRAMMICS) and from Cambridge will make it possible to identify and quantify multifunctional compounds in the organic aerosol and to find new markers.

Impact of carbon storage technology alkanolamines on new particle formation in air

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Key words: *methanesulfonic acid; new particle formation; alkanolamines; thermal desorption chemical ionization mass spectrometry*

Abstract: The energy landscape is changing worldwide, with a drastic reduction in sulfur dioxide (precursor to sulfuric acid, H_2SO_4) emitted from fossil fuel combustion. As a result, acid-base chemistry leading to new particle formation (NPF) from sulfuric acid is decreasing. At the same time, photooxidation of biogenic organosulfur compounds leading to the formation of H_2SO_4 and methanesulfonic acid (MSA) is expected to become more important. Aqueous solutions of alkanolamines have been proposed as carbon capture technology media to store carbon dioxide from stack plumes before release into the atmosphere. It is therefore expected that some of the alkanolamines will be released, making it critical to understand their atmospheric fates including their role in new particle formation and growth. We expanded our experimental studies of nucleation from the reaction of MSA with simple amines to the multifunctional alkanolamines, including mononethanolamine ($HO(CH_2)_2NH_2$; MEA) and 4-aminobutanol ($HO(CH_2)_4NH_2$; 4AB). Experiments were performed in a 1-m borosilicate flow reactor under dry conditions as well as in presence of water. These two systems were shown to produce sub-10 nm particles with MSA extremely efficiently. Surprisingly, the presence of water did not enhance NPF, in contrast to the drastic effect water had on small alkylamine reactions with MSA. This is likely due to the fact that MEA and 4AB have an -OH group that provides additional H-bond interactions within the cluster. Sampling of the chemical composition of these small nanoparticles with high resolution and high transmission was possible down to 3-4 nm using a novel high-flow differential mobility analyzer (half-mini DMA) interfaced to a thermal chemical ionization mass spectrometer (TDCIMS). There was no size dependence for the acid-to-base molar ratio (1:1) for either amine. Integration of these data with preliminary results obtained for a simple C4 alkylamine (butylamine) and a C4 diamine (putrescine) will be discussed in the context of developing a molecular structure-reactivity scheme for new particle formation from MSA and amines of varying structures.

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Quantifying the Mass Loading, Aging, and Cloud Properties of Polystyrene Nanoplastic Particles in the Atmosphere

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Key words: Atmospheric *Nanoplastic Particles, Aging, Real-time Chemical Characterization, Climate Properties*

Abstract: The prevalence of the nano- and microplastics detected in the ecosystem is an emerging problem worldwide. Nanoplastics have been shown to not only have adverse implications on human health and the ecosystem, but also contribute to climate forcing by efficiently scattering shortwave radiation and absorbing longwave radiation. Despite being increasingly important, there is no real-time online detection of atmospheric nanoplastic particles (NPP).

Herein, we provide the first study to quantify real-time nanoplastics concentrations in the atmosphere and their chemical reaction process. A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) is employed to detect submicron polystyrene (PS) particles, one of the most abundant microplastics produced. Several tracer ions, including m/z 74 and 104, are shown to be unique to PS particles. To validate whether this method can separate out PS particles from other ambient particles, PS particles are externally mixed with selected types of inorganic and secondary organic aerosols (SOA) in the laboratory. Ambient particles are also collected and analyzed by a constrained PMF (multilinear engine, ME-2) method to determine the temporal distribution of microplastic particles. A distinct factor that is highly correlated to the pure PS profile is separated. The mass concentration of PS nanoplastic particles is estimated to be 10-50 ng/m^3 with a detection limit of 3 ng/m^3 during our sampling in Houston.

In addition, the aging and lifetime of PS particles reacting with hydroxyl radicals (OH·), ozone, and UV light are characterized using a Potential Aersosol Mass (PAM) oxidation flow reactor. The pseudo first order rate constant of PS particles against OH$^{\cdot}$ radicals, k_{PS}, is calculated to be, 1.374×10^{-13} cm^3 molecule^{-1} s^{-1} while the ozonolysis and photolysis rates were negligible. Such results demonstrate that the main degradation pathway for MPP in the atmosphere is likely OH$^{\cdot}$ oxidation. Assuming an ambient OH$^{\cdot}$ concentration of 1×10^{6} cm^{-3}, the half-life time of microplastic in the atmosphere is estimated to be 84 days, significantly longer when compared with an average 2-week-lifetime of particulate matter in the atmosphere but shorter than their marine lifetime. Characterizing atmospheric NPP and their lifetime may bridge important gaps in understanding their long range transportation abilities, environmental persistence, health implications, and potential contribution to climate forcing.

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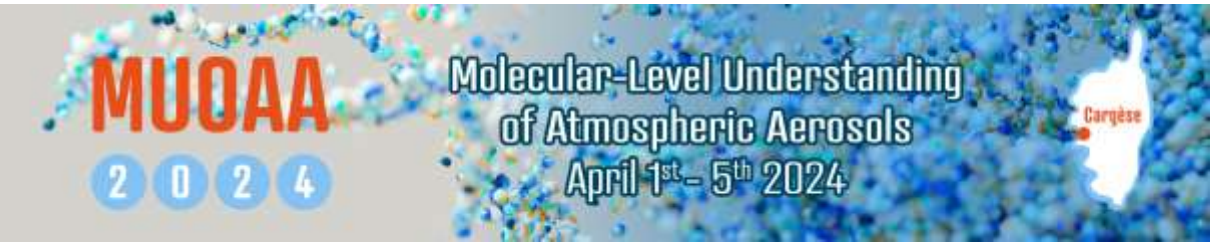

Abstracts - Posters

Nanodiamond Probes for Chemistry in Microdroplets

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Key words: *microdroplet, acceleration, interface, nanodiamond*

Abstract: Reaction acceleration in microdroplets is a current area of interest with implications for atmospheric modeling and green synthesis. A wide range of reactions have been shown to be accelerated by orders of magnitude in microdroplets as compared to the same reaction in bulk containers. This acceleration could be the result of a wide range of effects including electric fields, pH gradients, and evaporation. Separating out and measuring these effects is a difficult task leading to uncertainty in the exact mechanisms behind this reaction acceleration. Nanodiamond sensors with nitrogen-vacancy (NV) center defects are capable of measuring electric fields, magnetic fields, temperature, pH, and paramagnetic species quantitatively. Deploying these sensors in single levitated droplets, the concentration of gadolinium chloride has been accurately measured in microdroplets. These nanodiamond probes have additionally been used to quantitatively measure the rate of dissociation of Gd-DTPA in microdroplets under different pH conditions. Moving forward, these probes can separate out and quantify the contributing mechanisms behind reaction acceleration in microcompartments.

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Temperature Dependence of Criegee Intermediate-Driven Chemistry in Organic Aerosol

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Key words: *heterogeneous chemistry; ozonolysis; criegee intermediates; temperature dependence; aerosol mass spectrometry*

Abstract: The highly reactive Criegee Intermediate (CI) produced during ozonolysis of unsaturated compounds plays many significant roles in the oxidation of organic molecules in the atmosphere, such as initiating radical fragmentation chemistry or contributing to aerosol particle growth through oligomerization reactions. While direct-production measurements have enabled extensive gas phase kinetic studies of various CI reactions, the relevance of these gas phase measurements to chemical transformations in atmospheric aerosol, where reactant transport and surface processes likely play a non-negligible role in determining the reactivity, remains open to investigation.

To this end, we conduct temperature-controlled (253–293 K) aerosol flow tube studies of ozonolysis to probe the temperature-dependent branching ratios of various CI reactive sinks and constrain the kinetic parameters controlling organic aerosol aging processes across tropospherically-relevant temperatures. Reaction kinetics and product distributions are characterized using Vacuum Ultraviolet Photoionization Aerosol Mass Spectrometry, Atmospheric Pressure Chemical Ionization Mass Spectrometry, and particle size distribution measurements. Through exploratory kinetic modeling, we place constraints on the energy barriers to key reaction steps and find that a competition between CI unimolecular and bimolecular sink reactions, radical chain cycling chemistry, and ozone transport kinetics leads to a non-monotonic negative temperature dependence to the reactive uptake of ozone.

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MOCCA : a new platform to assess the multiphasic atmospheric organic chemistry with a Combipal - CHARON-PTR-ToF-MS

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Abstract

The atmosphere holds abundant organic matter, playing a dominant role globally (Noziere et al 2015). Understanding how organic compounds behave across different phases during the cloud life cycle remains a key inquiry. Throughout a cloud's existence, these compounds undergo efficient transformations via physical, chemical, and biological processes, dictating their distribution among cloud water, particles, and the gaseous phase.
However, grasping the fate of organic matter, especially in multiphasic atmospheres such as the pathways governing Secondary Organic Aerosol formation, faces limitations:

- Challenges in cloud sampling due to their sporadic nature.

- Limited observations at molecular levels in uncontrolled atmospheric conditions.

- Discovery of organic compounds in supersaturation within cloud water across various latitudes (Wang et al (2019) & Dominutti et al (2022)).

Introducing MOCCA (Mass spectrOmetry for the multiphasic Composition of the Cloudy Atmosphere), a novel mass spectrometry platform designed to characterize organic compositions in the gas, particle, and cloud water phases. MOCCA integrates a high-resolution PTR-ToF-MS (model 6000X2 IONICON Analytik GmbH, Austria), a CHARON inlet, and a temperature-controlled auto sampler (Combipal) to delve into the molecular-level composition of organic matter. Cloud water is collected using the BOOGIE cloud collector (Deguillaume et al 2024, in prep.) before analysis. The PTR-ToF-MS operates in H3O+ mode, scanning from 20 to 400 amu.

MOCCA's deployment spans diverse environments: a temperate suburban area (suburban Paris, SIRTA NF, France, ACROSS project), a subtropical forest site (São Paulo, Brazil, RMG, BIOMASP+ project), and the analysis at the CO-PDD NF (France) platform in a cloudy atmosphere (Cézeaux-Aulnat-Opme-puy de Dôme at 1465m a.s.l.).
Firstly, we will quantify the partitioning of species of interest between gas and particle phases

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*Speaker

in those environments. Secondly, we'll emphasize MOCCA's analytical capabilities in exploring the cloudy atmosphere with preliminary results on gas/cloud and aerosol/cloud phase partitioning observed in cloudy conditions and finally humidity effect on those processes.

Keywords: Multiphasic, Organic Matter, Partitioning, Mass Spectrometry

Influence of Amino Acid Structure on Phase Separation and CCN Activity in Ternary Mixtures

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Key words: CCN; Phase Separation; LLPS; Mixtures; Aerosol-Cloud Interactions

Abstract:

Aerosols are present as complex organic-inorganic mixtures within our atmosphere; and under certain conditions can exist with phase separated morphology. When submicron aerosols are exposed to supersaturated conditions (>100% RH), the water uptake ability of the aerosols vary based on the composition of the mixture. The hygroscopicity of complex mixtures presenting liquid -liquid phase separation LLPS was previously studied through the measurement of CCN activity within a 2-methylglutaric (2-MGA)/ammonium sulfate (AS) binary system and a 2-MGA/AS/sucrose ternary system; both studies correlated water-uptake abilities to O/C and surface tension. However, little is known about the influence of solubility of the third component on phase separation of a ternary mixture containing 2-MGA/AS. The water-uptake properties of mixtures containing nitrogen containing compounds, such as amino acids, are not well defined. Therefore, it is undetermined if O/C alone is an acceptable parameter for the estimation of solubility and hygroscopicity of complex amino acid mixtures. To improve our understanding of LLPS within aerosol mixtures and factors influencing its presence, three ternary systems were studied – a leucine system (2-MGA/AS/Leu), valine system (2-MGA/AS/Val), and proline system (2-MGA/AS/Pro). For each system, the CCN activity of mixture compositions with varying O/C ratios and compositions was measured using a Cloud Condensation Nuclei Counter (CCNC) from 0.3 to 1.5% supersaturation (SS). For all mixtures, the single hygroscopic parameter κ was calculated. Experimental κ results were compared against four theoretical models; three of the theoretical models included were Köhler theory, O/C LLPS with surface tension (O/C LLPS-ST) and a newly developed model, X/C LLPS with surface tension (X/C LLPS-ST). For this study, a new parameter considering O/C and nitrogen to carbon (N/C), X/C, was introduced as a parameterization for solubility. The O/C LLPS-ST model was adapted to consider X/C for subsequent estimations of κ. A fourth theoretical model took a weighted average of the O/C LLPS-ST and X/C LLPS-ST models. Each model provides insight into the complex nature of aerosol mixtures and subsequent droplet growth. Thus, this provides an improved understanding of organic nitrogen-containing aerosol mixtures' water uptake abilities through the introduction of new coupled parameter models. As a result, the study is able to show varied N/C contribution to the system based on the

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structure of the amino acid as well as a method to improve current abilities to predict hygroscopicity of these complex, nitrogen-containing aerosol mixtures.

KAOLINITE AEROSOL COMPLEX REFRACTIVE INDICES DETERMINATION FROM FAR INFRARED TO UV.

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Key words: Aerosols, Complex refractive indices, Mineral dust

Major injections of aerosols can have significant impacts on the radiative balance of the Earth. Quantifying these aerosols, from remote sensing techniques, is crucial to better identify their sources, monitor their atmospheric transport and understand their environmental impact. Satellite instruments like IASI for thermal infrared and FORUM for far infrared can provide important information about the chemical composition (Alalam et al. 2022) and microphysical parameters (concentration, mass, effective radius…) of these aerosols (Deguine et al. 2023). However, accurate information about the optical properties, specifically the complex refractive index (CRI), is required for these retrievals. Nevertheless, CRIs available in the literature have multiple limitations such as spanning over limited wavelength ranges and providing measurements on bulk materials which underestimate the scattering signal or pressed pellets samples that modify the vibrational modes. All these drawbacks limit their representativeness for the study of aerosols by remote-sensing techniques.

An improved retrieval methodology is presented, which combines experimental measurements for resuspended particles of high spectral-resolution extinction spectra (from 50 µm /200 cm^{-1} up to 0.25 µm /40,000 cm^{-1}) and the recording of the size distribution of particles. These data are then used in a numerical iterative process to retrieve the real and imaginary parts of the CRI using an optimal estimation method associated with the single subtractive Kramers-Kronig relation and scattering theories such as Rayleigh or Mie theory (Herbin et al. 2017).

This methodology has been applied to kaolinite, a clay found in mineral dust. The results show homogenous values of CRI retrieved continuously from far infrared to UV for suspended particles, addressing the limitations of traditional CRI databases.

Alalam, P., L. Deschutter, A. Al Choueiry, D. Petitprez, and H. Herbin. 2022. Aerosol Mineralogical Study Using Laboratory and IASI Measurements: Application to East Asian Deserts. *Remote Sensing* 14, no. 14 (January): 3422.

Deguine, A., D. Petitprez, L. Clarisse, L. Deschutter, K. Fontijn, and H. Herbin. 2023. Retrieval of Refractive Indices of Ten Volcanic Ash Samples in the Infrared, Visible and Ultraviolet Spectral Region. *Journal of Aerosol Science* 167 (January 1): 106100.

Herbin, H., O. Pujol, P. Hubert, and D. Petitprez. 2017. New Approach for the Determination of Aerosol Refractive Indices – Part I: Theoretical Bases and Numerical Methodology. *Journal of Quantitative Spectroscopy and Radiative Transfer* 200 (October 1): 311–319.

Application of Machine Learning for the Molecular Characterisation of Particle Formation

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Key words: secondary organic aerosols, machine learning, density functional theory

Abstract: The contribution of oxygenated organic molecules (OOM) to the formation of secondary organic aerosols (SOA) is known to be highly relevant, yet still poorly understood. Their experimental as well as computational investigation is impeded by the existence of myriads of different OOM, which makes their comprehensive molecular characterisation complex and costly. Yet, a large number of OOM also yields access to a lot of potential data, which can allow us to build robust computational models to understand the formation of SOA.

In our research we compute the stability and properties of OOM with density functional theory (DFT) and utilize the generated data, together with existing databases, to construct machine learning models that circumvent the computationally expensive calculation of these molecular properties. We focus on two key processes of SOA formation:

1) OOM can participate in the initial clustering of gaseous molecules in the atmosphere. We trained a neural network with data consisting of various OOM configurations generated with the JKCS suite (Kubecka et al., 2023) to predict the binding free energies, and thus minimum structures, of large OOM (130 – 150 atoms) clusters. We found that multiple OOM tend to curl into each other to maximize the number of stabilizing hydrogen-bonds between the different molecules.
2) Further, OOM drive particle growth beyond clustering via condensation. The affinity of OOM to condense to the particulate phase can be measured with respective saturation vapour pressures (p_{Sat}). We have conducted rigorous conformer sampling for 31,637 OOM, computed their p_{Sat}, and published them as the *GeckoQ* dataset (Besel et al., 2023). Moreover, we trained machine learning models on the generated data to predict p_{Sat} and employed these models for a targeted search of OOM with particularly low p_{Sat} in larger OOM datapools. To this end, we also explored active machine learning methods, where a dataset with a target property is assembled from scratch.

Overall, our work shows that data-driven methods are capable of predictions reliable enough to save significant computational resources, and can provide valuable insight into different stages of SOA formation. In future work, we hope to increase the size and variety of available datasets to build a comprehensive computational models that can predict SOA formation.

Kubečka J., Besel V., Neefjes I., Knattrup Y., Kurtén T., Vehkamäki H., and Elm J., *ACS Omega* *8* (47), 45115-45128 (2023)
Besel, V., Todorović, M., Kurtén, T., Rinke P., Vehkamäki H., *Sci Data* **10**, 450 (2023).

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Formation of Surface NaCl on a Sulfate-Rich Salt in Response to Water Adsorption

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Key words: *Particle surfaces; Desert salt; APXPS*

Abstract: Aerosolized salt particles emerge from several pathways and important continental sources include saline lakes and playas. Once in the atmosphere these particles play roles in atmospheric processes and are active multiphase materials due to their high hygroscopicity. Below deliquescence conditions, the surfaces of solvating material can exhibit unique chemical environments that differ from the bulk. The structure and properties of the gas-particle interfaces directly influence heterogeneous processes that are important to the atmosphere. In our study, the behavior of the gas interface of a natural salt sample collected in the Gobi Desert (East Asia) was investigated across a spectrum of Relative Humidity (RH). Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS), Near Edge X-ray Absorption Fine Structures (NEXAFS), and Molecular Dynamics (MD) simulations were used to examine in detail the salt's topmost molecular layers (≈ 1.5 nm depth). Ion chromatography (IC) was used to determine the salt's ionic bulk composition.

The ionic molar fractions obtained by IC (Table 1) show that the sample's anionic bulk composition is dominated by sulfate (SO_4^{2-}), with a molar fraction about 10 times higher than chloride (Cl^-). Contrastingly, our APXPS measurements, at RH = 0%, revealed that at the salt-gas interface, Cl^- is more enriched than SO_4^{2-}, but only at the salt's uppermost molecular layers (≈ 1.0 nm depth). When water vapor is added, at RH > 5.5%, a significant change in the probed depth studied (≈ 1.5 nm depth) is observed, where the abundance of Cl^- ions greatly increases and becomes 4 times more enriched than SO_4^{2-}. Complementary NEXAFS measurements revealed the formation of NaCl at the gas interface with increased RH. These findings emphasize that the interfacial composition of salts can be different from their bulk(s) and may change with changing water availability.

Table 1: Ionic composition of the Gobi Desert salt sample.

Ions	NO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	K^+	NH_4^+	Na^+
Molar Fraction	1%	39%	4%	6%	25%	1%	0%	39%

Role of surfactants in aerosol-cloud interactions: combining surface tension and partitioning models with analytical characterisation

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Key words: Surfactants, aerosol-cloud interactions, surface tension, surface-bulk-micelle partitioning

Abstract:

The role of surfactants in aerosol-cloud interactions is still debated. Their ability to deplete surface tension tends to enhance the CCN activity of the particle through Kelvin effect, whereas their partitioning between the bulk and the surface of the particle decreases the Raoult effect. Most of the studies conducted on this topic have used predictive models to investigate the partitioning and surface tension of surfactants in nanometer particles with high surface/volume ratio, but they have only considered model compounds. In the meantime, very few studies have explored the presence and characteristics of surfactants in atmospheric samples, and they have always been limited to bulk properties. This work aims at linking these two approaches. The objective is to feed comprehensive models adapted from the literature with results from a new analytical procedure for surfactants characterisation in atmospheric samples.

The analysis of atmospheric samples involves two steps. First, the mixture of surfactants is extracted from the sample using solid phase extraction (SPE), to measure the surface tension isotherm of the mixture with the pendant drop technique and drop shape analysis. Second, surfactants are quantified using a newly developed protocol including SPE followed by a spectrophotometric determination of a dye-surfactant complex extracted by liquid-liquid extraction. This second SPE involves four successive elutions to separate surfactants into four classes: cationic, non-ionic, weak anionic and strong anionic. This enables to reduce the interferences between cationic and non-ionic compounds observed in previously published protocols.

The information of the surface tension of surfactants as a function of the concentration in macroscopic drops, provided by the two analytical steps, is used as the input for three comprehensive models: Gibbsian, monolayer, and Langmuir frameworks. These models, used here in an inductive approach, account for partitioning of surfactants between the bulk and the surface, surface tension depletion, and micelles formation. The results are used to calculate both surface tension and partitioning of surfactants in nanometer particles, for implementation in the Köhler theory.

Results of surfactant concentrations from various surface water and atmospheric samples will be presented. Also, preliminary results of partitioning will be presented for model compounds, for comparison with the literature. This procedure will be used as a routine to compare the amount, characteristics and potential impacts on droplet formation of surfactants in atmospheric samples from various locations.

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Spontaneous formation of OH radicals and H_2O_2 in the air-water interface of water droplets at different temperature.

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Key words: Air-water interface, H_2O_2 formation, OH formation

Abstract: Aerosols are ubiquitous in troposphere. Due to their impact on human health, air quality and climate, the understanding of their physico-chemical properties is essential. There are many evidences that inside water droplets, hydrogen peroxide can be spontaneously formed. One possible explanation of this phenomenon is the presence of a strong electric field at the air-water interface. This electric field permits the dissociation of hydroxide anion into hydroxyl radical and an electron. Different mechanistic pathways can be proposed starting from this dissociation to explain the formation of hydrogen peroxide inside water droplets. Our study is focusing on this spontaneous formation and his impact in the oxidation of atmospheric aerosols.

Laboratory experiments have been done with differents instruments to measure the production of H_2O_2 and OH radicals. A nebulizer is used to generate water droplets in a range of 0.1-10 µm, from salt containing solutions. The size distribution of the droplets is obtained by an optical particle counter to have a correlation between size distribution and production of H_2O_2. After 30 minutes of experiments, the liquid gathered in a impactor is collected to measure H_2O_2 production with an H_2O_2 analyser. To investigate the role of temperature in the production of H_2O_2, the same experiment has been done at different temperature between 7°C and 24°C with different salts (NaCl, and NaBr). Furthermore, the production of OH radical has been detected in solutions with terephthalic acid (TA), an OH radical scavenger that produce a fluorescent molecule named as 2-hydroxyterephthalic acid (TAOH).

With this study, we have strong evidence that H_2O_2 is produced in the water droplets, and its concentration is estimated to be up to 1.10^{-1} µM, depending on the type of salt, the concentration and the size distribution of the generated particles. The temperature has an effect on H_2O_2 production different depending on the type of salt, that isn't understood yet. These results are expected to improve the physico-chemical properties of atmospheric droplets.

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Enhanced photochemical amide bond formation in optically levitated supersaturated aerosol droplets

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Key words: *(single particle; accelerated chemistry; supersaturation; prebiotic chemistry)*

Abstract:

The synthesis of peptides from amino acids is believed to have played a fundamental role in the origins of life. The reaction is generally thermodynamically unfavorable and therefore, unique geochemical environments have been invoked to elucidate possible abiotic mechanisms. Here we investigate the ability of aqueous aerosol particles to facilitate the condensation of amino acids in the presence of dicyandiamide, a hydrogen cyanide derivative. By monitoring the cavity-enhanced Raman scattering spectrum of single levitated droplets, the chemical and physical properties of the droplet can be monitored. We show that supersaturation in the droplet allows for the photochemical synthesis of peptides, driven by visible light irradiation from a dual-beam optical trap. The synthesis is very sensitive to initial droplet size, and the reaction rate kinetics provides insight into the reaction mechanism. This work demonstrates the potential for light-driven condensation reactions in aerosol droplets to facilitate prebiotic chemistry.

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Multiphase reactivities of excited states

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Key words: *Multiphase reaction, SO_2, excited states*

Abstract: Multiphase photosensitization in atmospheric aerosols has recently been proposed to induce a new oxidation pathway in the formation of secondary pollutants1. The photoexcitation of brown carbon (BrC) form excited triplet states of organic compounds (3C*) upon irradiation, which initiates the photosensitivity reaction occurring at the interface of aqueous aerosol, where the organic compounds may interact with gases or VOCs[2,3]. However, the mechanism and the multiphase process is still poorly known.

In this study, multiphase reactivities are illuminated by uptake coefficient (γ) of SO_2 using a Wetted-Wall Flow Tube (WWFT) in the dark and in the UVB (300-340nm). Aromatic carbonyls (like Vanillin, VL) and Humic acid (HA), as photosensitizer, are the main model compounds from biomass burning. The reactions were characterized based on decay kinetics, detected uptake, and the effect of photosensitizer concentration and temperature. It was confirmed that the uptake on VL(0-1mM) had a strong enhancement under the UV light, and no dark reaction was observed in our study as well as HA. The uptake coefficient (γ) of SO_2 linearly increased with VL at low concentration (0-0.2mM), and is eventually independent on VL concentration afterwards (0.2-1mM), the steady-state uptake coefficient is $(3.86 \pm 0.32) \times 10^{-5}$. The reactive rate of VL is 1.38×10^{9} M^{-1}. s^{-1}. At the concentration range of HA from 0 to 100 mg. L^{-1}, the uptake coefficient (γ) of SO_2 has a linear dependence with concentration of HA, and the variation range is 2.6-7.8×10^{-6}. The temperature is not an important effect on uptake of SO_2 in this work. Additionally, 1-octanol as a surfactant, shows the significant surfactant effect both on VL and HA. The products of reaction will be measured by LC-MS to reveal multiphase reaction mechanism.

Overall, this work reveals the importance of photosensitized reactions in the tropospheric condensed phase (i.e., cloud droplets and aerosols). It is a key for us to better understand and respond to the impact of biomass burning particulate matter on climate change.

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Coupling an acoustic levitator with a Raman microspectrometer and a proton-transfer-reaction mass spectrometer for studying single particle of atmospheric interest

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Key words: *Single atmospheric particles, acoustic levitation, spectroscopy, mass spectrometry*

Abstract: Single particle levitation techniques, which can suspend a particle of interest in a fluid medium, make use of electrodynamic, optical or acoustic forces[1]. More recently, acoustic levitation has attracted significant attention as it is minimally invasive, allows for a large volume of manipulation – which facilitates its coupling with other experimental instruments, and can operate with a wide variety of material samples[2]. The relevance of using acoustic levitation in the context of single aerosol particle chemistry has been demonstrated this last decade. [3-6] The experimental set-up we have developed consists in a commercial levitation device inserted in an environmental chamber and coupled first with a Raman microspectrometer (RMS) and second with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). The levitation –RMS set up allows to manipulate and probe individual particles under atmospheric conditions (i.e. temperature, relative humidity, pressure ….) when the coupling with the PTR-ToF-MS enable to measure the gas phase composition surrounding the individual particle. In this work, we will focus on two examples illustrating first the hygroscopic properties of model aerosol particles of atmospheric interest, for relative humidity varying between 10 % and 95 %. Our investigations have focused on the properties of 3 methyl-1,2,3-butanetricarboxylic acid (MBTCA), which is considered as a relevant molecular tracer for monoterpene BSOA formation and aging processes. The hygroscopic properties of single particles containing various concentrations of pure MBTCA, or in mixture with NaCl or $(NH_4)_2SO_4$, have been evaluated and agreed with some preliminary work[7] and with those calculated from the E-AIM thermodynamic model. In the second part, we will present the validation of the levitation-PTR-TOF-MS coupling, by following the gas composition during the evaporation process of a particle composed of a mixture of inorganic salt and linalool (3,7-dimethyl-1,6-octadien-3-ol).

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Reactivity, scattering, and energetic distribution of collisions between nitric oxide and oxidized graphite: Insights from AIMD calculations

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Key words

Ab initio molecular dynamics (AIMD), NO oxidation, activated carbonaceous surfaces

Abstract

Calibri Font 11 Justified Nitrogen monoxide (NO) belongs to the group of the most polluting gases in the atmosphere. It serves as a critical precursor for the formation of smog and acid rain, which currently pose significant environmental and human health challenges. Understanding the molecular interactions between NO and models of carbonaceous surfaces is essential for developing effective strategies to mitigate its adverse effects on the environment.

We presented here ab initio molecular dynamics (AIMD) calculations on the NO oxidation over oxygen functionalized High Oriented Pyrolytic Graphite (HOPG-O) surface. We examined the impact of four different NO incidence energies and two orientations of incidence on the reaction. Our simulation results indicate that the probability of the oxidation reaction (HOPG-O + NO(g) -> HOPG + NO2(g)) varies between 10-30%, depending on these initial conditions. Notably, the reaction occurs even at the lowest incidence energy studied (0.025 eV) which corresponds approximately to room temperature (300 K). The angular distribution of the products and the energy losses during the reaction were also analyzed. The scattered NO molecules (non-reactive channel), loses 50-60 % of their initial translational energy and are vibrationally cold but rotationally excited. The detected NO2 molecules share the same angular distribution as the scattered NO molecules, suggesting a swift and direct reaction dynamic for NO oxidation characterized by effective energy transfer. These findings provide important insights into the reaction mechanism of NO oxidation on activated carbonaceous surfaces, contributing to the potential development of applications to mitigate environmental pollution.

Molecular Dynamics Simulation of Freezing of Aqueous Alcohol Surfaces: Investigating the Isomer Effect

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Surface Active Organic Compounds (SAOCs) are preferentially adsorbed at the surface and are more exposed to incoming radicals and gaseous compounds. Significant research efforts have conducted to understand the role of these molecules in atmospheric processes, such as the formation of cloud condensation nuclei. However, less attention has been given to the impact of SAOCs on freezing processes. The present study is motivated by nanodroplet freezing experiments [1,2] that were best understood by considering the partitioning of these alcohols between the surface and the bulk. Here, classical molecular dynamics simulations have been performed to investigate the surface behavior of linear and branched alcohol isomers with different chain lengths, specifically 1-pentanol and 3-hexanol, and their impact on freezing. The results reveal a reduction in surface tension caused by the presence of the alcohol molecules at the interface. Moreover, as temperature decreases by approximately 50 K (283K→192K), surface tension increases and the solubility of both 3-hexanol and 1-pentanol increases. The present approach provides insights into how the molecular arrangement of different alcohol species within the interfacial zone affects freezing and ice formation.

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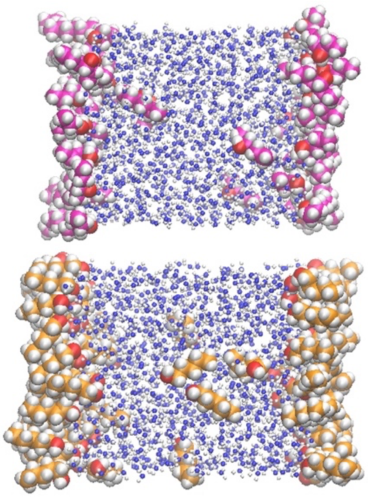

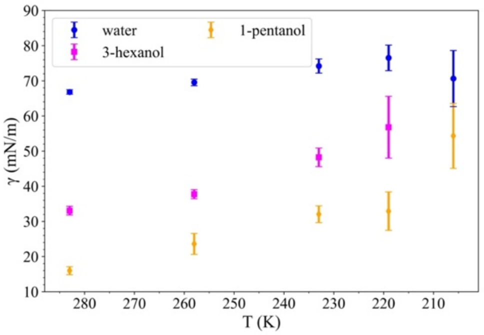

Molecular Dynamics Simulations of Chlorine Solvation in Squalene Aerosol

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Key words: *Molecular Dynamics; Air-Oil Interface; Kinetic Modeling; Organic Aerosol; Indoor Chemistry*

Abstract: The air/liquid interface is a distinct chemical environment that governs the uptake of gas-phase species into the aerosol bulk. We employ classical all-atom molecular dynamics (MD) to investigate chlorine adsorption at the squalene interface and subsequent solvation, quantifying the solvation free energy and mass accommodation coefficient. These are then used to construct a fully constrained kinetic model with no adjustable parameters to explain reaction kinetics observed in laboratory experiments.

We further utilize MD to obtain molecular-level information on an interesting experimental observation. Lab experiments have shown that the addition of oxygenated molecules accelerates the heterogeneous rate of squalene chlorination without altering the mechanism. By explicitly modeling the addition of alcohols to a squalene aerosol, we are able to explore the chemical distribution and probe the influence of alcohols on chlorine solvation and dynamics.

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BIOMASP+: Exploring SOA Formation from an Endemic Atlantic Forest Species under Ozone Stress Using an Oxidative Flow Reactor (OFR)

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Key words: SOA, megacity, ozone, oxidative flow reactor, vegetation chamber

Abstract : The oxidative processes occurring in the atmosphere play a key role in maintaining radical balance and influencing atmospheric composition. They facilitate the removal of volatile organic compounds (VOCs) and inorganic gases emitted by various life forms and human activities. Presently, over half of the global population resides in urban areas, where they encounter air pollution with anthropogenic emissions recognized as the primary source of pollution in megacities. However, evidence suggests that biogenic emissions can modulate the environmental and health impacts of anthropogenic pollution by acting as precursors (Shilling *et al.*, 2013).

Biogenic volatile organic compounds (BVOCs), which are stress-dependent, play a crucial role in this modulation (Faiola *et al.*, 2018). Thus, understanding BVOC emissions and SOA formation under O_3 stress in vegetation is of importance, particularly in urban areas where such interactions have significant implications.

The BIOMASP+ international project aims to evaluate the influence of biosphere-atmosphere interactions on gaseous and particulate urban pollution in São Paulo (SP), Brazil. As part of the BIOMASP+ project, this work focuses on BVOC emission and on the SOA formation. In order to study photochemical aging under controlled oxidative conditions (Peng and Jimenez, 2020), an Oxidative Flow Reactor (OFR) named Potential Aerosol Mass (PAM) OFR_{185} was used. The experimental set-up involved sequential sampling between a chamber environment and the PAM reactor via switching valves, coupled with a detailed characterization of the particle and gas-phases (ACSM, SMPS, CHARON-PTR-Tof-MS).

This set-up has been deployed at two sites, each with complementary objectives : one study ambient anthropogenic mix and the other on controlled conditions. The latter enables characterization of emissions and oxidation products of isoprene-emitting endemic species *Cassaeria Sylvestris* from the Atlantic forest ecosystem. This study was conducted at the Instituto de *Pesquisas Ambientais* (IPA) laboratory. And was carried out under O_3-induced emission conditions using a controlled vegetation chamber, focusing on a six-day exposure period to 90 ppb O_3 in a fumigation chamber, along with a corresponding control chamber.

This work potentially help better understand SOA yield *vs.* radical $OH^{\cdot}$ exposure (OH_{exp}), as well as described field and laboratory campaigns using PAM reactor.

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Studying the molecular properties of strongly or weakly bounded systems made of PAH and water for astrochemistry

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Key words: polycyclic aromatic hydrocarbons; molecular complexes and clusters; collision; photoexcitation; laboratory astrophysics

Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) and water molecules are ubiquitous in regions of star and planet formation in which they have an important contribution to the chemical evolution. In cold and dense regions, water molecules can adsorb on icy and carbonaceous grains containing PAHs. The irradiation by energetic photons or particles (cosmic rays) may lead to the formation of strongly bounded PAH-water complexes. The latter species correspond to PAHs in which oxygen has been incorporated, thus forming ketones, quinones or alcohols [1,2,3] which are key molecules in prebiotic chemistry. Exposure of the icy grains to UV irradiation may also lead to the evaporation of weakly bounded molecular clusters [4] thus enriching the molecular phase of these regions. Studying PAH-water systems in the laboratory by experiments and/or quantum chemistry is necessary to decipher their role in the chemistry of different astrophysical environments by comparison with astronomical observations.

We are investigating such topics thanks to a strong collaboration between three laboratories in Toulouse (IRAP, LCAR and LCPQ). This has led us to develop different methodologies to study mixed PAH-water systems. I will focus on the combined experimental techniques which permit us to produce, manipulate, isolate and study such species [5,6]. In general, the used sources generate cationic dehydrogenated, protonated or bare PAHs which act as nucleation seeds for the formation of clusters and the cluster growth proceeds by aggregation at low temperature with the surrounding water and/or PAH molecules. Thanks to different type of ion optics, we can select and isolate a given stoichiometry of these species (e.g. $[\mathrm{PAH}_n(\mathrm{H_2O})_m]^+$). The latter interact with colliders (rare gases or water molecules) or photons (from IR to VUV) which modifies their composition [7,8]. Thanks to mass spectrometry tools, we quantify these changes and have access to relevant parameters for astrochemistry (e.g. cross-sections). It also gives insights on fundamental processes such as photo-excitation and energy redistribution which are at play in astrophysical environments and may be of interest for atmospheric chemistry.

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The Effects of Acid-Catalyzed Multiphase Chemistry on the Hygroscopicity and Deposition Ice Nucleation of Complex Inorganic-Organic Mixed Aerosols

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Key words: *Multiphase Chemistry, Organosulfates, Hygroscopicity, Ice Nucleation*

Abstract:

The physicochemical properties of aerosols can significantly alter their cloud condensation and ice nucleation properties, as well as cloud microphysics. Among atmospheric aerosols, a significant fraction is coming from the multiphase reactions of biogenic volatile organic compounds (BVOCs) with anthropogenic acidic sulfate particles, leading to the formation of organosulfates. This study aims to bridge the scientific gap by investigating the impact of multiphase reactions on the phase state, mixing state, and morphology of the particles, and examining how the modification of the physicochemical properties would jointly affect the cloud condensation and ice nucleation activities.

The SOAs derived from four BVOCs are generated from a PNNL chamber, with both neutral ammonium sulfate (AS) and acidic ammonium bisulfate (ABS) seed particles. Both online and offline techniques are utilized to examine formation of OS through multiphase oxidation. Filter samples are collected, and the concentration and chemical composition of OS is determined by high resolution aerosol mass spectrometer and Nanospray Desorption Electrospray Ionization coupled with Orbitrap mass spectrometer. The SOAs are also collected onto the TEM grids with their morphology and phase state being analyzed with a Scanning Electron Microscope. The cloud condensation and ice nucleation (IN) activities of the SOAs undergoing multiphase reactions are measured by the PNNL Cloud Condensation Nucleus (CCN) Counter and the Continuous Flow Diffusion Chamber (CFDC) in real-time to derive hygroscopicity parameter κ and ice nucleation onset RH, respectively.

Our results show that the OS fraction is significantly higher for acidic seed particles for all four types of VOC precursor. The hygroscopicity of the SOA decreases as a function of organic coating thickness, even though the decrease is unequal for two types of seed particles. Using advanced source apportionment techniques, we separate the OS from inorganic sulfur, and demonstrate that SOA formed from multiphase reactions can significantly suppressing CCN and enhancing IN activities of

the particles, due to the formation of the OS. The results provide further insights in connecting multiphase reaction processes with aerosol-cloud properties.

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Notes