Water Uptake and Chemical Composition in Single Submicron Particles analyzed by X-ray Microspectroscopy

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Abstract

Aerosol particles, either from natural or anthropogenic sources, are important for atmospheric chemistry and the radiative balance of the atmosphere. Their influence on the climate originates mainly from the so-called 'direct effect' (absorption and scattering of radiation) and the 'indirect effect' (ability to act as cloud condensation nuclei). Hereby the chemical composition, the mixing state, the hygroscopicity i.e., the water amount associated with the particle at a given relative humidity, the physical state, and the microstructure in the case of mixed phase particles play all an important role. These properties are also affected by continuous chemical processing during the lifetime of the particles in the atmosphere.

The gross chemical composition of ambient aerosol particles has meanwhile been well established, even though many minor, especially organic compounds have not been identified. Typically, the single particles are a complex mixture of soluble, insoluble/refractory, organic and inorganic material. The physical state of such internal subphases within the particles are strongly linked to important questions in atmospheric chemistry and physics. For example, in aerosol chemistry reactive transformations of aerosol constituents by gas phase oxidants depend significantly on the microenvironment (e.g., solid/liquid) they are contained in. The microstructure and morphology of individual particles is also relevant for their optical properties (i.e., absorption and scattering).

We used scanning transmission x-ray microscopy, an imaging method which allows a spatial resolution of about 40 nm, for the analysis of single (sub)micrometer sized particles. In conjunction with x-ray absorption spectroscopy (XAS) spatially resolved chemical fingerprints of the samples can be obtained.

To probe the samples in an atmospherically relevant environment, we developed a microreactor, which allows to measure the samples in a well defined gas phase environment, specifically at well defined water vapor pressure and temperature. Therefore, this new measurement method enables to quantitatively visualize the water uptake within the samples depending on their chemical fingerprints.
To demonstrate the performance of our method, we observed deliquescence and efflorescence of single ammonium sulfate particles. XAS spectra of dry ammonium sulfate, its saturated, sub-saturated, and as a novelty, also supersaturated solutions were successfully used to reproduce the well-known humidogram of ammonium sulfate. Investigations on changes in microstructure upon water uptake were performed in mixed ammonium sulfate-adipic acid particles. These two compounds were shown to be immiscible at low relative humidity. At high humidity, the adipic acid was shown to exist as separate phase in an ammonium sulfate solution. In more complex organic mixtures, like Suwannee River Fulvic Acid, chemical functional group composition could be classified along their ability to take up water. The differences in water uptake ability in between different compound classes were so strong that spatial separation of these compounds was observed upon water uptake.

To study the effect of atmospheric aging on morphology and microchemistry of atmospheric particles, combustion particles emitted from two diesel cars and a wood stove were investigated before and after photochemical processing in a smog chamber. The comparison of unprocessed and aged soot reveals changes in their chemical composition, which presumably stemmed from direct oxidation by gas phase oxidants and the condensation of organic compounds produced by oxidation of gas phase precursors. These changes were shown to be directly related to the increased water uptake ability. The direct oxidation of soot under the effect of ozone and light was also investigated in a separate study. The results show that the combination of UV or visible light with ozone changes the chemical composition of soot particles in a way that water wettability was decreased.

Within this work we could demonstrate that scanning transmission x-ray microscopy and absorption spectroscopy can be used to address the relation between microchemistry and water uptake behavior in materials of atmospheric relevance. Using the nanofocus of the x-ray microscope these investigations could be conducted in single particles with sizes larger than 150 nm to mainly address particle to particle variations, while for particles larger than 400 nm investigations on the internal chemical arrangements could be conducted. Therefore, this method allows obtaining important morphological information under atmospheric conditions as input into future estimates of essential aerosol parameters, such as the optical properties of particles.
Zusammenfassung


Um die Mikrostruktur solcher Teilchen auf einer submikrometer Skala abzubilden wurde ein Röntgenmikroskop mit einer Auflösung von 40 nm eingesetzt. Ein solches Mikroskop kann mit Röntgenabsorptionsspektroskopie kombiniert werden, so dass räumlich hochaufgelöste, chemische Signaturen in einzelnen Partikeln gemessen werden können.

Damit einzelne deponierte Aerosolteilchen in einer atmosphärisch relevanten Gasphasenumgebung gemessen werden können bzw. deren Verhalten auf Veränderungen z.B. der relativen Feuchte oder Temperatur, wurde ein sogenannter Mikroreaktor gebaut. Die Röntgenabsorptionsspektroskopie- und mikroskopie ermöglicht dann die Veränderungen in den Partikeln, welche z.B. durch die Wasseraufnahme entstehen, quantitativ zu visualisieren aber auch spektroskopisch nachzuweisen.


In dieser Arbeit wurde das Röntgenmikroskop and die Röntgenabsorptionsspektroskopie dazu verwendet, um Zusammenhänge zwischen der Mikrochemie und der Wasseraufnahmefähigkeit von atmosphärisch relevanten Substanzen aufzuzeigen. Der Gebrauch von einem Röntgenmikroskop ermöglichte dabei die Untersuchung an Einzelpartikeln (>150 nm) zu realisieren bzw. interne chemische Strukturen zu analysieren bei Proben in der Größenordnung von 400 nm und mehr.
Chapter 1

Introduction and Outline

In this chapter, general aspects of aerosols and their importance for climate are discussed. The contribution of morphology, phase state and hygroscopicity to the climate effects of aerosol particles are addressed, along with methods to access these experimentally. This chapter concludes with a discussion about soot.

1.1 Aerosols - an introduction

Aerosol particles are defined as a suspension of solid particles or liquid droplets in a gas. They are emitted either from natural sources, e.g. volcanoes, deserts, arid areas, oceans, or from anthropogenic sources such as byproducts from incomplete combustion of fossil fuels (Figure 1.1). Two kinds of aerosol particles, differentiated by their formation processes, are observed: primary particles emitted directly as particles, and secondary particles formed in the atmosphere by gas to particle conversion processes e.g. by oxidation [Seinfeld and Pandis, 1997]. The majority of aerosol particles are found in the troposphere. A small fraction of them can be found in the stratosphere after heavy volcanic eruptions. They may remain for several months because of missing removal processes. The aerosol particles in the stratosphere induce colorful sunsets (see Figure 1.2) by scattering shortwave radiation, whereby blue and violet wavelengths are also scattered (Rayleigh scattering) by nitrogen and oxygen in the atmosphere. Strong scattering of light in the atmosphere causes a 'whitening' of the sky. Besides their influence on the color of the sky, aerosol particles raise many questions about their effect on human health or climate. In the discussion about the climate effect of aerosol particles, two major influences can be identified. On the one hand aerosol particles scatter and absorb shortwave/longwave radiation, thus they alter the radiative balance of the atmosphere. This effect is known as direct aerosol effect. Many parameters exist, which circumscribe this effect. Some of these are the
Chapter 1. Introduction and Outline

Figure 1.1: Sources of aerosols (aging, anthropogenic and natural sources) and their possible fates in the atmosphere

specific extinction coefficient (absorption of light per unit path length), or the single scattering albedo (ratio of scattering efficiency to total extinction efficiency, which is also called "attenuance"). An example for an absorbing particle is black carbon, which heats up the atmosphere. Most other organic aerosols scatter the solar radiation and thereby cool the atmosphere [Kanakidou et al., 2005]. These absorption/scattering properties depend not only on the aerosol type but also strongly on the environment the aerosols are incorporated in. These are among other things relative humidity (RH), e.g. dry particles do not scatter as well as when they are in deliquesced form [Martin, 2000], or atmospheric loading.

On the other hand, aerosol particles can act as cloud condensation nuclei, such that the particles grow to fog or cloud droplets. Hence, they can modify the microphysical properties of clouds and affect so their amount and lifetime [Novakov and Penner, 1993], usually referred to as the indirect aerosol effect. Important parameters are chemical composition, size distribution, mixing state or ambient environment. A high uncertainty of about a factor of 3 remains related due to these forcings [Kanakidou et al., 2005].
1.2 Chemical composition

As stated before the chemical composition of aerosol particles is an important factor which influences the impact on their atmospheric forcings. The pie charts in Figure 1.3 shows the mass proportion of the chemical composition in aerosol particles at various sampling locations, in urban areas (a) and alpine sites (b) [Pöschl, 2005]. As visible in this illustration the composition of aerosol particles varies quite strongly with their sampling location. Other studies found that the composition of fine particulate matter in rural areas in the U.S. consists of 20-40 % of organic material whereas in urban areas a contribution of 30-80 % was found [Jacobson et al., 2000], and in tropical forested areas the organic matter contributes with almost 90 % to the total mass [Kanakidou et al., 2005]. Most of the organic mass in the aerosols was shown to be water soluble. Decesari et al. found the fraction of water soluble compounds to be 77 % of the total organic mass [Decesari and Fuzzi, 2000].

Also visible in Figure 1.3, inorganic compounds constitute for another high fraction of the aerosol mass. Major constituents are sulfate, nitrate and ammonium. A different substantial fraction of tropospheric aerosol particles are soot particles. They are important constituents in the atmosphere because of their complex role in climate [Ackerman et al., 2000] due to their long range transport [Ramanathan et al., 2001], and their complex aging, which includes particle oxidation, coating and agglomeration with e.g.
sulfates [Fuller et al., 1999], see also below. A separate section below is devoted to generation, chemical properties and atmospheric aging of soot particles.

1.3 Morphology of aerosol particles

The morphology of aerosol particles is of importance because of its influence on human health [Katrinak et al., 1993] and its influence on absorption/scattering properties of light [Martins et al., 1998]. Since the composition of aerosol particles varies strongly depending on the emission source and the particle processing in the atmosphere, also the appearance i.e. morphology [Bond and Bergstrom, 2006], which includes size, shape and internal structuring of the compounds, is quite inhomogeneous. Ebert et al. [Ebert et al., ] divides atmospheric particles on the basis of morphology and chemical composition into ten different groups. The shape of these particles varies from spheres (silicate sphere, iron oxide sphere), cubic (sea salt), agglomerates (soot) or to not well defined structures (carbonate).

Atmospheric particles are assumed to form also mixed phases (liquid and/or solid) [Ravishankara, 1997]. According to Weis and Ewing [Weis and Ewing, 1999], and Colberg et al. [Colberg et al., 2004] eight different groups can be differentiated in mixed solid and/or liquid particles: single crystal, agglomerate of single crystals or polycrystalline solid, polycrystalline material with several open cavities filled with liquid, a solid polycrystalline shell with embedded liquid, single solid crystal with surrounding liquid, polycrystalline solid with surrounding liquid and liquid aerosol particle. However, a liquid particle consisting of two immiscible liquid phases can form three possible configurations: complete engulfing of aqueous phase by the organic phase, partial engulfing of the aqueous phase and nonengulfing [Kwamen et al., 2010].

It is clear that all these different morphologies influence in different ways the climate by changing the properties of aerosol particles as scatterer or absorber, or may impact their chemical properties. As already mentioned, the liquid droplets show higher scattering ability than dry aerosol particles. But also heterogeneous inclusions of e.g. soot in ammonium sulfate particles strongly affect the scattering/ ab-

![Figure 1.3: Pie charts illustrate the chemical composition with their typical mass proportion in a) urban and b) high alpine air. The charts were adapted from Pöschl (Pöschl, 2005).](image)
sorption of aerosol particles. Hereby the soot component increases the absorption but decreases the scattering compared to ammonium sulfate which leads to a significant reduction of the single scattering albedo and leads to decreased cooling effect of the sulfate aerosols [Worringen et al., 2008, Chýlek et al., 1995]. These effects depend on the size of the inclusions of soot or ammonium sulfate [Chýlek et al., 1995]. But very often the morphology of the single particles is unknown and the scattering behavior can not be modeled in a way that the calculated data would fit the experimental values [Lang-Yona et al., 2010]. Even the scattering behavior of a two-component mixture like adipic acid and ammonium sulfate was not possible to model correctly, also in this case it was explained by the unknown morphology [Freedman et al., 2009].

Another example, where morphology plays an important role, are marine aerosols, which are known to have coatings with amphiphilic molecules like long chain carboxylic acids [Tervahattu et al., 2002b, Tervahattu et al., 2002a]. Such coatings may impact the chemical, physical and optical properties of aerosols [Facchini et al., 2000]. The organic coatings may lower the surface tension of wet aerosols, whereby evaporation, condensation and gas dissolution are influenced [Facchini et al., 2000]. Additionally, it was shown that the physicochemical state of such coatings is important. Hearn et al. [Hearn and Smith, 2007] could show in the oxidation reaction of oleic acid by ozone in a n-docosane matrix that after a partial, incomplete reaction of this unsaturated acid with ozone an inhibition of further oxidation of oleic acid with ozone was observed, although oleic acid is known to be rapidly oxidizable by ozone. The formation of a metastable solid rotator phase of the n-docosane at the surface was suggested. Hearn et al. suggest that this phase could slow down the diffusion of ozone into the particle such that the reaction is inhibited. This behavior of docosane was not observed when the docosane formed the thermodynamically stable triclinic solid.

The importance of the physical state was shown in another example, the depletion of $N_2O_5$. It was shown that the uptake of this trace gas is higher in liquid droplets than in solid aerosol particles [Hallenquist et al., 2003]. Therefore, the knowledge on the physical state is also important to estimate the partitioning and reactivity of gas-phase species between the gas and the condensed phase [Kocifaj et al., 2006, Laurain and Reid, 2009].

These examples illustrate the importance of the knowledge of chemically resolved morphologies in aerosol particles. Thus, this work helps to estimate the impact of particles of complex morphology in atmospheric processes.
1.4 Water uptake in aerosol particles

1.4.1 General

As stated before, the physical state of aerosol particles plays a crucial role in partitioning of trace gases as well as absorption/scattering properties of aerosols. Water uptake in response to varying ambient humidity, which can drastically change the morphology of aerosol particles, is therefore an important factor in aerosol science. The water uptake ability of single particles depends mainly on the chemical composition which varies with the location as discussed before. Organic and inorganic compounds may show a so called deliquescence (sudden water uptake) and efflorescence (water loss) behavior. Table 1.1 shows examples for the deliquescence RH (DRH) and the efflorescence RH (ERH) of pure compounds. Deliquescence is called the point during humidity increase where the dry compound suddenly starts to transform into a saturated solution. At this point the Gibbs free energy of the solid salt becomes equal to the energy of the saturated salt solution. Further increase of humidity leads to additional increase of the water amount in the solution in order to maintain thermodynamic equilibrium [Seinfeld and Pandis, 1997]. The efflorescence behavior is shown during decreasing humidity, whereby the solution looses water and becomes supersaturated when passing the DRH. The solution remains supersaturated until the efflorescence point is reached where the compound nucleates. This nucleation is usually far lower in RH than the deliquescence point because an energy barrier has to be overcome for nucleation. Note that this behavior is contrary to the deliquescence where no energy barrier has to be overcome. Figure 1.4 shows single aerosol particles before and after deliquescence measured at the PolLux beamline with the scanning transmission x-ray microscope (see below). An example for an inorganic substance, which does not show deliquescence/efflorescence behavior is

Table 1.1: Deliquescence relative humidities [Brooks et al., 2002, Parsons et al., 2004, Peng et al., 2001, Sjogren et al., 2007, Tang and Fung, 1997]

<table>
<thead>
<tr>
<th>Pure compound in water</th>
<th>DRH [%]</th>
<th>ERH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>81.7</td>
<td>35</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>75.7</td>
<td>44</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>87.5</td>
<td>29 - 33</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>74.3</td>
<td>no</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>93.0</td>
<td>51.8 - 56.7</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>87.5</td>
<td>10</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>91.0</td>
<td>55.2 - 59.3</td>
</tr>
</tbody>
</table>
1.4. Water uptake in aerosol particles

Sulfuric acid. This acid shows continuous water uptake, since it forms stable solutions with water at most atmospherically relevant humidities and temperature (except for the formation of hydrates at low T).

![Image of sodium chloride particles deposited on the silicon nitrate membrane at different RH levels](image)

**Figure 1.4**: Images measured at 538 eV of sodium chloride particles deposited on the silicon nitrate membrane at 60 % RH (left) and 76 % (right), the color bar indicates the OD (optical density) values, all images were normalized according to the Lambert-Beer law.

1.4.2 Methods to map water associated in (aerosol) particles

A variety of techniques is applied to study the amount of water taken up by (aerosol) particles. Bulk measurements are highly accurate, but provide only data on saturated and dilute solutions. Under atmospheric conditions widely supersaturated solutions are expected [Kanakidou et al., 2005], therefore the quantitative amount of water taken up by different compounds is usually observed with suspended solution particles.

A common instrument to determine the water uptake ability of aerosol particles is the Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) [Mikhailov et al., 2004]. Using this instrument, data can be obtained on the hygroscopic growth of a large number of dry aerosol particles of a chosen size (submicrometer sized particles) at defined RH. In general, the aerosol hygroscopicity is expressed with the growth factor, which is calculated from the ratio of the measured diameter of the humidified aerosol particle and that of its dry particle, see Figure 1.5.

In pure substances the growth factors can be theoretically calculated, if the concentration of the solute material is known as a function of the water vapor pressure ratio (partial pressure of water vapor divided by saturation water vapor pressure) over the particle surface [Kanakidou et al., 2005]. For small particles (less than few hundreds of nm) a correction factor has to be introduced, the so-called Kelvin-term [Russell and Ming, 2002].

A different method to monitor the water uptake for a particle ensemble of an aerosol plume is the nephelometer. This instrument detects the amount of light scattered by the particles. Variations in scattered light intensity are assumed to be proportional to the aerosol mass concentration [Benton-
Figure 1.5: Humidogram of ammonium sulfate adapted from Sjogren et al. [Sjogren et al., 2007], the different stages of the water uptake/release are marked: 1. no water uptake, 2. water uptake after deliquescence was reached, 3. water release

Vitz and Volckens, 2008]. Humidograms of ammonium sulfate are constructed from the amount of scattered light [Dougle et al., 1998].

Another technique to gain information on growth of particles upon water uptake is the Electrodynamic Balance (EDB) [Peng et al., 2001, Treuel et al., 2008, Marcolli and Krieger, 2006], which is usually combined with a spectroscopic method like Raman. The EDB captures one single charged particle in an electric field, whereby the size of these particles is in the range of several micrometers. With the EDB experiments on the scattering properties of aerosols were reported [Davis and Ravindran, 1982], also the diameter (and refractive index) of the particles can be calculated. Studies using Raman spectroscopy on the water uptake of single levitated particles were also reported, see [Musick et al., 1999]. Mapping of the water uptake is performed by following the OH stretching in the raman spectrum at around 3400 cm\(^{-1}\).

The particle growth upon water uptake can also be studied by direct observation using an optical microscope, but again only particles of several micrometers can be measured. Usually, this is combined with Raman spectroscopy, which gives additional information on the chemistry of the particles [Yeung et al., 2009].

Measurements with an Environmental Transmission Electron Microscope (ETEM) or an Environmental Scanning Electron Microscope (ESEM) give the possibility to measure submicron particles with a certain vapor pressure, such that also water absorbed by the particles can be mapped [Ebert et al., 2002]. ETEM also gives the possibility to perform spectroscopic analysis on the single particles using EELS (Electron Energy-Loss Spectroscopy), see also chapter 2. However, few studies are so far published using EELS for in situ water uptake and release measurements [Gajdardziska-Josifovska and Sharma, 2005, Sharma, 2001]. As discussed later on, the beam damage is strong when the electron microscope is used, such that samples may be chemically altered under the effect of the electron beam.
This may limit the usage in the context of atmospheric particles somewhat. AFM (Atomic Force Microscopy) is also a common imaging method to study single submicron particles [Posfai et al., 1998]. In contrast to electron microscopy, the AFM studies can be performed under atmospheric conditions. It is a nondestructive method since only the topography of the particles is scanned. The AFM gives also the possibility to study hydrated substrates. Disadvantages here are e.g. the small area accessible to scanning, longer scanning time or artifacts, which can evolve during the scanning.

Overall, two basic concepts were introduced here, the measurement of an aerosol plume and single particle analysis. The advantage of single particle studies is clearly that supplementary information on the particles can be afforded beside the growth factors, like evolution of morphology as well as spectroscopic information on the single particle providing information about particle to particle variation that cannot be retrieved from ensemble methods. A drawback in these single particle measurement methods is the low statistics, which is inferior even if hundreds of particles are measured [Takahama, 2007], compared to HTDMA measurements, where thousands of particles are scanned.

To investigate chemically resolved morphologies, we used x-ray microscopy in combination with x-ray absorption spectroscopy. Chapter 2 is dedicated on the description of this method. However, this combination gave us the possibility to perform spatially resolved spectroscopy on submicron particles. In comparison with EELS the x-ray absorption spectroscopy does not damage the sample so strongly. Therefore reliable, high-quality spectra are possible to obtain; for particle to particle variations, see also the humidogram in chapter 3. Advantageously, x-ray can penetrate to a certain extent wet samples. Therefore, this combination allowed us to map also water in particles. To study such water uptake effects in situ on single particles, a microreactor was built, which allows to control the gas phase environment of deposited particles. This setup in combination with x-ray absorption/microscopy allowed quantitative mapping of water associated in submicron particles along with visualization of morphological changes, characterized using their chemical fingerprints. Thus, such measurements provide important input to model physical properties of atmospheric aerosol particles.

1.5 Soot

1.5.1 Soot formation

The methodological development of this thesis was linked to a project dealing with the characterization of soot particles from diesel vehicles with different exhaust aftertreatment technology, NEADS (Next generation exhaust aftertreatment devices) of the Center of Excellence of Energy and Mobility, CCEM-CH. Therefore, a separate section is devoted here to a general introduction to formation and
aging of soot particles.

Soot is formed by incomplete combustion of fuels. Anthropogenic as well as biogenic sources are known as origins for soot. It consists of black carbon, which is named due to its light absorbing properties, and organic components. These components (e.g. polyaromatic hydrocarbons, PAH) influence the scattering as well as the nucleation properties of soot. If soot particles consist of enough hygroscopic material, they can act also as cloud condensation nuclei. As depicted in Figure 1.6, soot particles consist of primary, spherical particles agglomerated to large structure. Usually, these agglomerated particles can have a size of a few hundred nanometers up to a few micrometers [Vernooij et al., 2009, van Poppel et al., 2005, Kis et al., 2006]. As shown in Figure 1.7 several steps are involved in soot formation, which has still remained relatively uncertain. Good overviews on the formation of soot are given by Appel [Appel et al., 2000], Frenklach [Frenklach, 2002], Haynes [Haynes and Wagner, 1981], Kennedy [Kennedy, 1997] and Wang [Wang and Frenklach, 1997].

The most accepted model for soot formation is via polycyclic aromatic hydrocarbons [Frenklach, 2002]. The first step in formation of soot particles is the pyrolysis of the fuel forming the precursor compounds like acetylene or methane radicals. Different possibilities of precursor compounds are feasible, see [Frenklach, 2002, Wang and Frenklach, 1997] and references therein. These preliminary compounds form aromatic compounds with e.g.

\[ nC_4H_3 + C_2H_2 \rightarrow \text{phenyl}, \]  

(1.1)

which was shown to be a key reaction in the formation of aromatic compounds [Frenklach, 2002]. However, as considered by Frenklach, there is still an ongoing discussion about the major preliminary compounds. Different other authors stated the preliminary compounds to be the propargyl radical with

\[ C_3H_3 + C_3H_3 \rightarrow \text{benzene or phenyl} + H, \]  

(1.2)
which was found to be thermodynamically more stable than the even-carbon-compound, which transforms to their iso-forms [Miller and Meltus, 1992]. Besides these formation mechanisms several other mechanisms are suggested, which will not be discussed here but can be reviewed in the literature cited above.

After formation of aromatic compounds, polycyclic aromatic hydrocarbons (PAH) are formed. It seems that the abstraction of a H radical with a subsequent polymerization is most favorable. Two examples are given: The propagation of the polymerization by addition of aromatic radicals

\[
\text{C}_5 + \text{C}_5 \rightarrow \text{C}_{10}
\]

(1.3)

and the addition of acetylene.

\[
\text{C}_5 \text{C}_5 + \equiv \rightarrow \text{C}_{12}
\]

(1.4)
Note that one major feature of these reactions is the reversibility of the $\text{H}^-$ abstraction.

$$
\begin{align*}
\left[ \text{C}_n \right] + \text{H}^- & \rightleftharpoons \left[ \text{C}_n \right]^* + \text{H}^- \\
\end{align*}
$$

(1.5)

The repetitive $\text{H}^-$ abstraction and addition of a gaseous acetylene molecule is known as HACA (‘H-abstraction-C\textsubscript{2}H\textsubscript{2}-addition’) reaction sequence. Additionally to the aromatic growth, the oxidation of these intermediates is propagated usually by $\text{O}_2$. The oxidation of the compounds is usually found at the beginning of the soot formation because oxygen is consumed by the $\text{H}$ radical so that at a prolonged reaction time, oxygen is not available anymore.

The chemical growth of the small preliminary compounds to PAH’s is followed by the collision of the PAH species which stick together and form polymers. During the collision the PAH’s keep on growing via chemical growth, which continues until solid particles are formed. Such particles can continue growing via acetylene addition [Dobbins et al., 1995] to aromatic structures.

These solid particles can coalesce i.e. collide with each other and form larger particles. During coalescence, the so-called coalescence-phenomenon can occur. Here, two particles can completely merge into each other like liquid droplets. However, this tends to happen only to small, freshly generated particles. In general, only partial restructuring is observed forming the neck region bridging the two particles together in a chain-like structure.

### 1.5.2 Aging of soot particles

When soot particles are emitted to the atmosphere, they experience aging. This process is important for the absorption, scattering and lifetime properties in the atmosphere. For example, it was shown that condensation of organic compounds on soot particles can increase their scattering and absorption ability [Xue, 2009]. The same effect was observed with sulfates [Fuller et al., 1999]. However, such hydrophilic coatings decrease the lifetime of soot particles [Adachi et al., 2007] by faster wash out, where soot particles with their hygroscopic coating act as cloud condensation nuclei [Dusek et al., 2006]. Further processes like agglomeration with e.g. sulfates [Khalizov et al., 2009], oxidation, or restructuring [Abel et al., 2003, Khalizov et al., 2009, Pagels et al., 2009] are observed. Since soot is widely assumed to be insoluble in water as well as in organic substances when emitted, such atmospheric processing increases the CCN ability of soot [Andreae and Gelencser, 2006, Deccesari et al., 2002, Deccesari et al., 2006].

Oxidation of soot by ozone can occur through addition to double bonds via the Criegee mechanism [Smith et al., 1988, Criegee, 1975]: After a cycloaddition of ozone to the double bond, the primary
ozonide is decomposed to the Criegee intermediates—a carbonyl compound and a carbonyl oxide [Criegee, 1975]. These intermediates can react via a cycloaddition to the secondary ozonide. However, the release of CO$_2$ and CO is observed during exposure of soot to ozone [Smith et al., 1988, Grundmann et al., 2005]. This is explained by decarboxylation of the Criegee intermediate with one residue being a functionalized residue like hydroxide or alcohol in presence of small ozone concentrations [Smith et al., 1988]. At high ozone concentration higher amount of CO$_2$ and CO are produced through less selective reactions [Smith et al., 1988], see also chapter 6.

A different, important aging mechanism of soot is the reaction with hydroxyl radicals [George and Abbatt, 2010]. Although the OH· concentration is very low (during daytime: 1-10·10$^6$ molecules cm$^{-3}$), the reaction rate is fast, which makes this compound an important constituent in the aging mechanism. This aging mechanism takes place mostly during the day since the hydroxyl radicals are formed by photodissociation of ozone, HONO, HCHO and H$_2$O$_2$ [Seinfeld and Pandis, 1997]. The ozonolysis of alkenes is another, non photochemical mechanism to generate hydroxyl radicals. OH· can abstract an H· from alkanes such that alkyl radicals are formed. These so formed alkyl radicals can then undergo a reaction with oxygen to form peroxy radicals which can decompose or react further with NO or HO$_2$ [Atkinson, 1997]. Unsaturated compounds, alkenes, do not experience the hydrogen radical abstraction first but the OH radical directly adds to the double bond. This hydroxy radical can then undergo the same reaction pathways as described for alkanes [Atkinson, 1997].

Still open is the influence of such aging mechanisms on the CCN ability of soot. It has been observed that not all oxidation processes necessarily lead to an increase in CCN activity, therefore other aging mechanisms like the coating of SOA seems to be the more important mechanism for CCN activation [Moffet and Prather, 2009].
1.5.3 Interaction of soot with water

The elemental composition of soot is typically about 85-95 % C, 3-8 % O, and 1-3 % H by weight [Clague et al., 1999, Ferry et al., 2002]. However, these numbers give the impression that soot is a solid with graphitic nature and only low water affinity. But since most of the oxygen is found on the soot particle surface, the particles do not behave like graphite. Therefore, the water is not expected to show a strong diffusion into the primary particles but remains rather on the surface. Several possibilities are feasible for water interaction with soot particles [Popovicheva et al., 2008]: a) water adsorption on a few hydrophilic sites, b) Langmuir or BET type adsorption though hydrophobic interactions, c) formation of a solution with (in)organic solutes present on the surface.

Also here, different methods can be applied to measure water uptake, most of them are discussed in chapter 1.4. Often, HTDMA has been applied to measure water uptake. While very small growth factors at high humidity have been reported in some cases, most often a shrinking of the particle size is observed due to restructuring of the particle [Weingartner et al., 1997]. Usually, the particle growth/shrinking is between 0 and 5%. The restructuring is explained by water, which condenses in small angle cavities of the particle under subsaturated conditions. This condensation leads to capillary forces in the branches of the aggregates, which causes them to collapse [Weingartner et al., 1997]. Besides HTDMA measurements also ETEM [Semeniuk et al., 2007] measurements were performed. Changes in structure were observed too, but the large beam damage impeded the analysis of organic compounds.

1.6 Contribution of this work to the development of methods dedicated to microstructure and morphology, and the understanding of processes at different gas phase environments on micrometer sized particles - Outline

As stated above, the physical and chemical properties of aerosols are very inhomogeneous and not well understood [Jimenez et al., 2009], but on these properties their climate effects depend on. The extent to which the aerosol particle influence climate is very much depending on the environmental conditions to which the particles are exposed. Additionally, as the aerosol particles are usually a complex mixture of different compounds, the complex interplay between individual components as a function of humidity and as a result of atmospheric oxidation processes including the formation of separate phases, especially in internally mixed organic / inorganic particles, is just poorly understood. Therefore, accurate identification of the behavior of the single components or phases within individual
particles during the uptake and release of water is necessary. This has been the primary motivation to develop an in situ x-ray microspectroscopic method to observe water uptake, morphology and chemical composition in submicron particles with submicrometer resolution. The aim of this thesis was to develop this technique and demonstrate its performance and capabilities for a variety of single component systems, well defined but also more complex mixtures such as humic like material or soot from different combustion sources. The results - the interplay between morphology, chemical composition and hygroscopic properties - may be then be further used as input to assess climate relevant physical properties of aerosol particles.

As an example for an atmospheric oxidation process, the oxidation of soot and its consequences on microstructure and hygroscopic properties at the single particle level was investigated in more detail. This included kinetic experiments in flow tubes, oxidation experiments in a smog chamber as well as offline x-ray spectroscopic analysis of particle samples from these experiments.

This work gives insights into water uptake behavior of single submicron particles and characterization of single particles during aging using x-ray microspectroscopy. The water uptake behavior is shown to depend on aging of the particles, on their chemical composition and on the environment. This thesis is organized as follows:

**Introduction**  Gives a general overview on aerosol particles and their relevance for the atmosphere. Morphology issues relevant for climate, water uptake behavior of aerosol particles and especially of soot are discussed.

**Methods**  The interaction of x-ray with matter and the PolLux beamline with its end station are introduced; the microreactor with the flow system and sampling methods are shown. A short discussion on data processing is added.

**Direct observation of water uptake and release in individual submicrometer sized ammonium sulfate and ammonium sulfate/adipic acid particles using x-ray microspectroscopy**  This chapter gives first results on microscopy and spectroscopy of the water uptake in ammonium sulfate and ammonium sulfate/adipic acid submicron particles.

**Humidity driven nanoscale chemical separation in complex organic matter**  In this chapter complex mixtures and their water uptake behavior were investigated. Quantitative water uptake is shown as function of functional groups.
Aging fingerprints in combustion particles  The characterization of soot particles which were aged under more atmospheric relevant conditions is shown. These experiments were conducted in a smog chamber. Also here the water uptake capability of fresh and aged soot was investigated.

UV/Vis radiation increases steady-state uptake of ozone on soot  Here, the kinetics of the soot aging were investigated upon ozone uptake in dark and during irradiation. This study should demonstrate the soot degradation upon ozone exposure solely.
Bibliography


Chapter 2

Methods

This chapter gives an introduction into x-ray absorption spectroscopy and microscopy. For further reading, the books from Stöhr [Stöhr, 1992], Bachrach [Bachrach, 1992] and the Italian physical society [Mob, 2001] are recommended. The chapter concludes with a short discussion on the data processing and a description of the microreactor we used in conjunction with x-ray microspectroscopy.

A more detailed description of the microreactor and performance test has been published in

An in situ cell to study phase transitions in individual aerosol particles on a substrate using scanning transmission x-ray microspectroscopy

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2.1 X-ray interaction with matter

The interaction of photons with matter depends on the elemental composition of the sample and on the energy of the incoming photon. Monoenergetic photons pass through a medium and are attenuated according to the relation

\[ I(E) = I_0 \exp^{-\mu_l(E)d}, \]  

which is known as the Lambert-Beer law. Here, \( \mu_l \) defines the linear attenuation coefficient, which depends on the x-ray energy \( E \), sample composition and density, and \( d \) the thickness of the sample. The linear attenuation coefficient is related to the mass absorption coefficient via the equation

\[ \mu_l = \rho \sum_i g_i \frac{\mu_i}{\rho}. \]  

\( g_i \) denotes the atom fraction of the \( i \)-th species, \( \mu_i/\rho \) the mass attenuation coefficient and \( \rho \) the density of the material. Figure 2.1 illustrates the theoretical cross section of carbon over a range of \( 10^{-2}-10^8 \) keV. Different kind of interactions of photons with matter can be identified: elastic scattering (Rayleigh scattering), inelastic scattering (Compton scattering), pair production and photoelectric effect (Hertz Effect). The photoelectric effect dominates the interaction with matter in the range of soft x-rays (100-1000 eV). Therefore, for further discussion, the other effects will be neglected.

![Figure 2.1: Theoretical and measured cross section of carbon, with \( \sigma_{pe} \) being the contribution from the photoeffect, \( \sigma_{el} \) from elastic scattering, \( \sigma_{inel} \) from inelastic scattering and \( \sigma_{pp} \) from pair production. Adapted from [Arndt et al., 2006]
2.2 X-ray absorption

The photoabsorption process results in an excited system. After excitation the system can undergo relaxation into the deexcited state via different processes: The emission of a fluorescent photon or the emission of an Auger electron, which originates from the decay of another valence electron into the core shell transferring the decay energy to a valence electron, see Figure 2.2. Both deexcitation processes can be detected. Other ways to detect the photoabsorption process are the detection of photoemitted electrons in function of their kinetic energy (total electron yield, TEY or partial electron yield, PEY) or the measurement of the attenuation of the beam passing through the sample as a function of the incoming photon energy.

![Diagram](image.png)

**Figure 2.2:** Processes, which can undergo due to attenuation of an x-ray photon. The core electron is excited into a energetically higher state (an unoccupied molecular orbital) or removed from the molecule (ionization). In case of ionization the core electron is emitted as photoelectron, which can be detected (TEY, PEY). The deexcitation of the system is then concluded by different ways: fluorescence (left) or emission of an Auger electron (right).

2.2.1 Fine structure of the x-ray absorption

The absorption coefficient is a smooth function depending on the photon energy, which is interrupted by discontinuities, the so-called absorption edges, see Figure 2.1 and 2.3. These edges are observed when the energy of the photons is high enough to transfer a core level electron into vacuum (ionization) or excite it to an unoccupied molecular orbital. The latter case results in resonance absorptions at
Chapter 2. Methods

2.2 Spectroscopy at the carbon K-edge and oxygen K-edge

Using NEXFAS spectroscopy specific atomic species can be selectively probed. Examples for different atomic species absorbing in the soft x-ray region are shown in Figure 2.3. As visible in this Figure, important atmospherically relevant elements are covered by the soft x-ray regime, which makes this technique suitable for analysis of such particles. However, in this work we focus on the carbon and oxy-
2.3 PolLux

2.3.1 The beamline

The experiments were conducted at a synchrotron radiation source, the SLS (Swiss Light Source) located at the Paul Scherrer Institut (PSI). It operates at a beam energy of 2.4 GeV and electron current of 400 mA. The experiments using NEXAFS spectroscopy were conducted at the PolLux microscope. The microscope was built by J. Raabe and coworkers [Raabe et al., 2008]; similar to the original concept of Kirz and Rarback [Kirz and Rarback, 1985], this microscope builds on the version realized earlier at the ALS (Advanced Light Source) [Warwick et al., 1998, Kilcoyne et al., 2003].

Table 2.1: Transition energies of the fine structure at the carbon edge [Cody et al., 1998]

<table>
<thead>
<tr>
<th>Energy [eV]</th>
<th>Transition</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>283.7</td>
<td>1s→π*</td>
<td>Quinone</td>
</tr>
<tr>
<td>284.9-285.5</td>
<td>1s→π*</td>
<td>Aromatics</td>
</tr>
<tr>
<td>285.8-286.4</td>
<td>1s→π*</td>
<td>O-Aryl, Carbonyl substituted aromatic</td>
</tr>
<tr>
<td>287.7-288.3</td>
<td>1s→π*</td>
<td>C=O</td>
</tr>
<tr>
<td>287.6-288.2</td>
<td>1s→σ*</td>
<td>CH₃, CH₂, CH</td>
</tr>
<tr>
<td>288.2-288.6</td>
<td>1s→π*</td>
<td>COOH</td>
</tr>
<tr>
<td>289.3-289.5</td>
<td>1s→σ*</td>
<td>C-OH</td>
</tr>
</tbody>
</table>

Table 2.2: Transition energies of the fine structure at the oxygen edge [Hopkins et al., 2010]

<table>
<thead>
<tr>
<th>Energy [eV]</th>
<th>Transition</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>530.1</td>
<td>1s-π*</td>
<td>Benzoquinone</td>
</tr>
<tr>
<td>531-532</td>
<td>1s-π*</td>
<td>carboxyl, ketone</td>
</tr>
<tr>
<td>533.4</td>
<td>1s-σ*</td>
<td>C-OH</td>
</tr>
<tr>
<td>538</td>
<td>1s-σ*</td>
<td>Ketone, alcohol, phenol</td>
</tr>
</tbody>
</table>

Table 2.1 and 2.2 show important transition energies with specific chemical functional groups in the carbon and oxygen spectra. Figure 2.4 shows NEXAFS C K-edge spectra of different organic compounds. Spectrum a) shows anthraquinone, b) perylene, c) stearic acid, d) oleic acid and e) maleic acid. Different functional groups can be identified, compare with table 2.1 and references [Oji et al., 1996, Francis and Hitchcock, 1992, Outka et al., 1987, Ishii and Hitchcock, 1988].
Figure 2.4: Examples showing different organics to demonstrate the capability of NEXAFS spectroscopy to monitor different chemical functionalities. Spectrum a) depicts anthraquinone, b) perylene, c) stearic acid, d) oleic acid and e) maleic acid. All spectra were measured without the high order suppressor.

A schematic setup of the PolLux beamline with the end station is shown in Figure 2.5. To obtain the highest possible flux of electromagnetic radiation covering a broad range of energies, a synchrotron source is used. The radiation source from the beamline is a bending magnet. The beam is refocussed using a torodial mirror in the horizontal plane. Passing the entrance slit the electromagnetic radiation is diffracted at a grating. The exit slit behind this grating serves to 'pick' a small energy range from the diffracted light. A high order suppressor was installed behind the monochromator to guarantee monochromatic x-rays. It consists of three mirrors. The scattering angle of these mirrors can be chosen such that only photons of the desired energy are reflected. By this method high order contribution from the diffraction grating in the monochromator are suppressed.

The end station is separated from the beamline by a silicon nitride membrane. The whole beamline is
kept at about $10^{-9}$ mbar. For further details concerning the PolLux beamline, see [Raabe et al., 2008].

**Figure 2.5:** Overview of the setup at the Pollux beamline without the high order suppressor but with its end station, the scanning transmission x-ray microscope; the microscope is shown with the ZP (zone plate) and OSA (order sorting aperture)

### 2.3.2 The PolLux end station

The PolLux end station is equipped with a scanning transmission x-ray microscope (STXM). The STXM consists of a Fresnel zone plate (ZP), an order selecting aperture (OSA), a raster scan sample holder (x and y, and z direction for focusing purposes) and a detector for the light which has transmitted the sample. The ZP is the focusing element in the x-ray microscope. It consists of grates (alternating transparent and opaque) which focusses the x-ray via diffraction to a small spot size, see Figure 2.6. To eliminate the undiffracted (zero order) light, a central stop in the ZP is introduced, aligned with the OSA, which is located between the ZP and the sample (Figure 2.6). The sample is scanned in the focal plane of the beam in x and y direction to obtain microscopic images (see below). The transmitted photons are measured by a detector placed as close as possible behind the sample. Measuring the intensity of the transmitted light as function of the energy allows to take NEXAFS spectra of the sample.

### 2.3.3 Measuring Modes

Using STXM, different kind of measurements can be performed: conventional spectroscopy, microscopy and microspectroscopy.

**Spectroscopy** In the conventional spectroscopy the sample is usually placed in the focus of the beam
whereas photons of defined energy transmit the sample. Different possibilities are available to measure a spectrum (see also Figure 2.7):

**Point scans.** One single point on the sample window is defined, where the measurement should be performed. While the energy is increased with the defined step size refocussing in the horizontal direction the transmission data is acquired at this point. To normalize the acquired spectrum according to the Lambert-Beer equation (equation 2.1) a spectrum has to be measured on a sample free region on the window.

**Line scans.** Instead of a point, a line can be specified through the sample whereby the x and y coordinates of the sample are changed according to the defined line. An advantage of this measurement mode is that the line can be defined such that it covers both sample and sample free region so that $I_0$ is measured simultaneously. This measurement mode includes already some spatial resolution.

**Microscopy** At a fixed energy the sample is placed in the focus of the beam. Typically, an area of interest is chosen so that the sample is scanned in the focus of the beam along the x and y coordinate at the prescribed spatial resolution. Different kinds of information can be obtained with such microscopic images:

**Absorption maps.** The absorption map is an normalized image (according to the Lambert-Beer law) which shows the absorption at the chosen energy. Because all elements absorb a finite amount of light at any energy, one can observe the net distribution of the sample depending on the sum of the individual cross section of the elements.

**Chemical maps.** In this processed image the distribution of a specific element and its chemical func-
tional group can be observed, respectively. This information is obtained by measuring at two different energies: one image is taken before an absorption edge for background subtraction and the second one is taken at the energy of the absorption edge of the element. Both images are converted to absorption images using the Lambert-Beer equation and afterwards subtracted from each other.

Microspectroscopy The term ‘microspectroscopy’ refers to a technique where spectroscopic information on a sub micrometer scale is obtained. Hereby "image-stacks", developed by Jacobsen et al. [Jacobsen et al., 2000], are recorded. The image-stack is a series of images measured at different energy step sizes, usually of 0.1-0.5 eV. This means that from each measured pixel a spectrum can be extracted. Depending on the chosen spatial and energy resolution, long waiting times (up to several hours) need to be taken into account. All spectra and images can be analyzed using aXis2000, as implemented by Hitchcock et al. (Hitchcock 1997). For the alignment of the single images in the image-stack and the image analysis own routines were written, some morphological operators are described in the following paragraph.

![Figure 2.7: The different possibilities to gain spectroscopic information depicted, a) point scan, b) linescan, c) stack](image)

2.4 Image processing

For further reading the book 'Image processing using Matlab' from Gonzalez [Gonzalez et al., 1987] is recommended.

A problem of the images measured without high order suppressor was the low contrast due to the presence of additional high energy radiation which pretended high transmission. To increase the problem additionally, high intensity absorptions from electron injections into the electron storage ring complicated the image processing and alignment, see Figure 2.8.

To perform a reliable image alignment several morphological operations were necessary, see Figure 2.9:

- To get rid of the high absorption intensities caused by the electron injections the images were
Figure 2.8: Soot particle with high intensity electron absorptions

filtered using a standard running average filter.

- The images were converted first into binary images using an empirically determined threshold $th$, i.e.

$$ Ib(i,j) = \begin{cases} 
0 & \text{if } Im(i,j) < th, \\
1 & \text{if } Im(i,j) \geq th.
\end{cases} \quad (2.3) $$

Here, $Ib$ denotes the binarized image, $Im$ the source image and $(i,j)$ the coordinate relative to the upper left corner of the image.

- To isolate the absorption of the single particles a so called morphological opening was applied. The opening of a binary image $A$ by a structuring element (SE) $B$ is defined as

$$ A \odot B = (A \ominus B) \oplus B \quad (2.4) $$

which defines an erosion of $A$ by $B$ followed by dilation of the eroded image by $B$. An erosion is a morphological process which 'shrinks' objects in a image. The shrinking is controlled by the SE whereby the SE is chosen to be an object smaller than the investigated particle. For exact definition of erosion and dilation, the reader is referred to Gonzalez et al. [Gonzalez et al., 1987]. The dilation 'grows' an object in a binary image using the chosen SE. In this way the object in the image resizes again to the original size.

- Using these binary images the center of mass $C_m$ of the isolated particle was defined as

$$ C_m = \frac{\sum_{(i,j)} Ib(i,j)r(i,j)}{\sum_{(i,j)} Ib(i,j)}, \quad (2.5) $$

where $r(i,j) = \sqrt{i^2 + j^2}$ is the distance to the origin of the coordinate system. The translational offset was then determined based on a defined template image.

- The images were finally shifted according to the calculated offset.
However, these procedures are reliable for isolated particles only. As soon as absorbing objects were covering large areas or large structures were investigated, normalized cross correlation was alternatively applied for image alignment, whereby gray-scaled images were used.

![Figure 2.9](image)

**Figure 2.9:** Different stages of image processing showing a) inverted original image with adapted color bar, b) the filtered image, c) the opened image.

## 2.5 The Experimental Setup

### The Microreactor

![Figure 2.10](image)

**Figure 2.10:** left: Front of the microreactor with 1. the copper cooling wire, which is connected to the liquid nitrogen dewar, 2. the heating, 3. the sample holder of the microreactor, where the aerosol particles are deposited (inside); right: the back of the microreactor with 4. the body of the reactor comprising the second window (5.), the gas in- and outlet (6.) and 7. the temperature sensor, which allowed temperature measurement.

The microreactor, see also Figure 2.10, was built to enable measurements of deposited aerosol particles in a defined gas phase composition, similar to other cells used in x-ray studies [Neuhausler et al.,]
Chapter 2. Methods

To ensure fast and convenient handling the microreactor was built consisting of two parts: The body of the reactor, which implements the gas inlet and outlet and the sample holder, where the sample is placed. To enable the transmission of x-rays the reactor possesses two parallel silicon nitride windows. The window size of one window is 1 x 1 mm, mounted at the body of the reactor, and the window size of the second 0.5 x 0.5 mm, fixed at the sample holder. These different window sizes have a practicable reason: due to the smaller size of the sample holder window the focussing is always performed on the small window, where the sample is placed. Both windows have a thickness of 50 nm and are about 300 µm apart from each other.

Figure 2.11: Microreactor in the microscope; 1 cooling of reactor with liquid nitrogen; 2 gas supply for reactor; 3 heating device for the reactor with temperature control; 4 sample holder of reactor; 5 zone plate focuses the x-ray beam to the sample probe; 6 OSA (order sorting aperture); 7 detector

An important factor is the temperature in the reactor during the measurements. The temperature \( T_{\text{reactor}} < T_{\text{chamber}} \) is assessed by cooling the reactor with liquid nitrogen which is filled into a dewar attached to the microscope chamber. This dewar is connected via a copper wire and aluminum block to the reactor. To reach the desired temperature, the microreactor is heated to the defined temperature which is measured with a temperature sensor fixed close to the sample holder. Because of the low heat conductivity of the gas phase, it is necessary to pump the STXM chamber to low pressures \( 10^{-5} \text{ bar} \) to ensure that there is an insulation vacuum around the reactor. Since the two windows of the wafer could not withstand large pressure differences, it is necessary to lower the pressure in the microreactor. It was found that 150 mbar is a suitable pressure in the reactor.
2.5. The Experimental Setup

The Flow System

Figure 2.12: Illustration of the flow system used to control the gas phase composition in the reactor

The flow system enables to control the gas phase composition and pressure in the reactor. The composition of the flow is adjusted by mixing two variable flows of helium, whereby one flow passes a temperature controlled humidifier. When experiments were conducted with a different temperature in the reactor than room temperature, the humidity was recalculated in the microreactor using Michell Instruments (Cambridgeshire, UK) since the humidity sensors were located outside the microscope chamber. The humidity in the chamber was measured using capacity sensors at the inlet and outlet of the microreactor. Stable conditions were reached when the difference of the two sensors was in the range of ±2 %. This difference in RH occurs due to a pressure drop over the microreactor under the typical flow conditions of ~20 ml/min.

An example of oxygen K-edge spectra of dry and deliquesced NaCl and NaNO$_3$ submicron particles is shown in Figure 2.13, respectively. NaCl (left) does not show any absorption at 0 % RH, red spectrum, since no oxygen is present under this conditions. But at 82 % RH after water uptake, black spectrum, a clear absorption similar to water is measured. NaNO$_3$ (right) shows at 0 % RH beside the $\sigma^*$ absorption around 540 eV also a strong $\pi^*$ absorption at around 532.5 eV, upper spectrum, which is still visible at 80 % RH after deliquescence of NaNO$_3$, lower spectrum. Within error of the RH measurement, deliquescence occurs always at RHs consistent with literature values confirming proper performance of the system. More details are given in Huthwelker et al. for the case of NaBr [Huthwelker et al., 2007].

Sample Preparation

For the sample preparation various methods were developed, each to fulfill different requirements. These are the nebulizer for preparation of submicron particles, sampling from the smog chamber, the microdispenser for very low sample volume and dry films.
Chapter 2. Methods

Figure 2.13: Left panel: O K-edge spectra of deposited NaCl aerosol particle at 50 % (red spectrum) and 82 % RH (black spectrum), right panel: spectra of NaNO$_3$ (as well prepared via the aerosol method, see also below) at 0 % RH, upper spectrum, and 80 % RH, lower spectrum

Nebulizer method  For the preparation of submicron particles a homebuild aerosol generator was used. Using ultrasound, a freshly prepared solution was nebulized. Hereby, a piezoelectric transducer transmits its vibrations to the solution in the nebulizer chamber and causes cavities at the surface layer. Finally a nitrogen flow of 1.5 l/min separated solution droplets from the bulk solution. The generated aerosol particles were lead through a silica gel dryer, where the solution droplets were dried. Before the particles were deposited electrostatically (voltage 0.8 keV) the particles were charged using a so called corona charger, see also Figure 2.14. This corona charger ionizes gas molecules, which attach to the generated aerosol particles.

Sampling from smog chamber  The smog chamber is a 27 m$^3$ teflon bag where atmospheric processing can be simulated, see [Chirico et al., 2010]. Four arc xenone lamps with a cutoff at 280 nm simulate sunlight. Emission particles of different diesel cars (a EURO 2 transporter and a EURO 3 passenger car) and a wood stove burner were sampled.

From an outlet line at the smog chamber the aerosol particle were sampled. The corona charger system was also used for this sampling. The particle concentrations in the smog chamber were low (10$^4$ $\mu g$/cm$^3$) so that the sampling took several hours, see chapter 6.
2.5. The Experimental Setup

Figure 2.14: Left panel: the upper image shows the impactor with the sampling device, the lower image shows the sample holder of the microreactor mounted on the sampling device. Right panel: the whole impactor setup with the corona charger (1.) and the impactor (2.) are shown.

**Microdispenser method**  The microdispenser is a piezodriven syringe provided by GeSim (Gesellschaft für Silizium-Mikrosysteme mbH) operated by U. Krieger et al. at ETHZ. The microdispenser was used to produce solution droplets of about 60-180 picoliters, which were deposited on the silicon nitride window of the membrane such that the sample holder was placed on a x/y movable microstage. While generating the droplets, the stage was moved in x and y such that a pattern of droplets was generated. In contrast to the nebulizer method, where the particles were in a range of 200-800 nm in size, the microdispenser method provides droplet residue sizes of about 10-30 µm. The droplets were deposited in their aqueous state in contrast to the nebulizer method where the aerosol particles were dried before deposition on the sample window.

This method is preferred for samples where only little volume (0.3-1 ml) is available, which would not be sufficient for operation of the nebulizer. In contrast to the bulk samples (see below) this method gives controlled droplets and ensures that there is still free membrane for $I_0$ measurements.

**Bulk samples**  Few samples were also prepared by drying a droplet (usually few microliters) on the sample holder. This method results in samples for which the thickness cannot be well controlled
so that optically thin enough sample locations and sample free region for $I_0$ measurements are more difficult to find.

### 2.6 Limitations of the technique

Different limitations of the STXM-NEXAFS method can be specified:

- **Beam damage** Compounds suffer from damage when exposed to the photon beam. Depending on the sample, the extent of beam damage may vary strongly. An example is shown in Figure 2.15 which shows anthraquinone after multiple exposures to the beam. Here the decrease of the $\pi^*_{C=O}$ absorption (288.3 eV) can be observed as well as a decrease in thickness of the sample (305 eV). Therefore, each sample needs a measurement protocol to ensure lowest beam damage.

![Figure 2.15: Linescans of anthraquinone, these line scans were measured with step sizes of 0.08 eV and a dwell time of 4 ms. The black spectrum was measured first, followed by the grey, light grey third and the blue one. Visible is the strong decrease of the $\pi^*_{C=O}$ absorption at around 288.3 eV. A small decrease is also observed in the $\pi^*_{C=O}$ transition at 284 eV, a slight larger decrease is observed at the transition of $\pi^*_{C=O}$ and $\pi^*_{C=C}$ at 286 eV [Francis and Hitchcock, 1992].](image)

- **Long measurement times** Measurements of image stacks with a high spatial resolution can take several hours. This limits the amount of investigated particles to 10-30 per sample.

- **Sample thickness** Since the transmitted light intensity is measured, the thickness of the sample is restricted.

- **Dirt in the chamber** Measurements at low temperature (i.e. $<0\,^{\circ}\mathrm{C}$) can cause problems when the microscope chamber is not very clean. Dirt can condense on the sample holder and may disturb the measurements. Figure 2.16 shows such condensations marked with a black arrow, the optical
thicker anthraquinone is marked with a grey arrow. The corresponding spectrum of dirt is shown in the right panel of Figure 2.16.

![Image](image.png)

**Figure 2.16:** Left panel: transmission image of an anthraquinone sample measured at 300 eV. The compounds with lower OD, marked with a black arrow, indicate the condensed dirt, anthraquinone is marked with a grey arrow. Although the sample was measured at 295 K, a condensation of dirt was observed, which shows that during this measurement the microscope chamber was exceptionally dirty. Right panel: shows the corresponding spectrum of the low absorbing substance.

### 2.7 Electron Energy Loss Spectroscopy (EELS), a comparison

As discussed in chapter 1, ETEM/ESEM in combination with EELS offers as well the possibility to combine an imaging method in the submicron regime with spectroscopy. EELS uses an electron beam with a known kinetic energy. The energy loss of the electrons is measured after they passed the specimen. This loss can be caused due to inelastic scattering by innershell and outershell electrons. The innershell excitation give rise to ionization steps. By inspecting this ionization step a similar fine structure as in NEXAFS spectra can be observed. A great disadvantage is that most of the electrons are damaging the sample [Braun et al., 2005] and just a low fraction is associated with core level excitation [Hitchcock et al., 2008]. Rightor et al. showed that this damaging is about 100-1000 times larger than in NEXAFS [Rightor et al., 1997] [Hitchcock et al., 2008]. This radiation damage makes the method difficult to use for soft matter because of the ease with which chemical bonds break due to electrons. Another disadvantage when compared to the NEXAFS spectroscopy is the low energetic resolution of EELS. However, concerning the spatial resolution of the two techniques TEM-EELS is preferred [Egerton and Malac, 2005]. While STXM can measure with a spatial resolution of 15 nm, using TEM a resolution of a few Angstrom resolution may be reached. The main advantage of x-ray spectroscopy is that x-rays can pass through gaseous environments (at atmospheric pressure) and can pass also through fully hy-
drated samples, so that the study of samples with about up to a few µm thickness is possible [Egerton and Malac, 2005] [Hitchcock et al., 2008]. The combination of NEXAFS with STXM is therefore well suited for environmental samples, especially in conjunction with our microreactor allowing in situ studies under wet conditions.
Bibliography


Chapter 3

Direct observation of water uptake and release in individual submicrometer sized ammonium sulfate and ammonium sulfate/adipic acid particles using x-ray microspectroscopy

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3.1 Abstract

Scanning transmission x-ray microscopy (STXM), a microscopy method which allows imaging with a spatial resolution of 40 nm, and x-ray absorption spectroscopy were used to follow in situ the water uptake and release in submicrometer sized particles on a substrate enclosed in a microreactor. Oxygen K-edge near edge x-ray absorption fine structure (NEXAFS) spectra from supported ammonium sulfate particles in their dry salt, saturated solution and supersaturated solution states were obtained for the first time. The variations at the oxygen edge were related to the water content as a function of relative humidity (RH), consistent with mass growth measurements done on larger samples or suspended particle ensembles. Investigations on morphological changes upon water uptake were performed in mixed ammonium sulfate-adipic acid particles using STXM images and NEXAFS spectra taken at the oxygen and carbon absorption edges, confirming the two phase structure suspected from previous hygroscopicity studies, where adipic acid forms a separate phase of complex morphology partially enclosed by the ammonium sulfate solution at high RH. This example emphasizes the combination of chemical resolution provided via NEXAFS, spatial resolution via STXM and the in situ capability provided by the novel microreactor to obtain information about the microstructure of mixed organic/inorganic particles under close to ambient conditions.

3.2 Introduction

Aerosol particles from natural and anthropogenic sources are important for atmospheric chemistry, the radiative balance of the atmosphere, and also human health. The influence of the aerosol on the climate is mainly divided up into two categories: the direct effects and the indirect effects. The direct effects are related to the optical properties of the particles. The indirect effects depend on the ability of the particles to act as cloud condensation nuclei (CCN). Both, optical properties and CCN ability, are a function of the chemical composition, the mixing state, the amount of water taken up at a given relative humidity (RH) i.e., hygroscopicity, the phase state, and the microstructure in the case of mixed phase particles. These parameters are similarly important in the effect of aerosol particles on atmospheric chemistry or human health.

The rough chemical composition of ambient aerosol particles has meanwhile been well established, even though many minor, especially organic compounds, have not been identified in detail. Single particle mass spectrometry applied to many locations in the atmosphere has established that aerosol particles are typically internally mixed, indicating that the individual particles are a complex mixture of soluble, insoluble/refractory, organic and inorganic material [Haywood and Boucher, 2000]. With respect to hygroscopic properties, for both, typical major organic and inorganic constituents, water
uptake and release by individual compounds has been investigated [Sjogren et al., 2007]. A number of studies have been performed with particles of mixed inorganic/organic composition, e.g. [Sjogren et al., 2007, Hameri et al., 2002, Braban and Abbatt, 2004, Mikhailov et al., 2004, Brooks et al., 2003]. For such mixtures, methods have been developed to predict the amount of water associated with a particle in equilibrium with a given RH. Such studies on mixed compositions also emphasized the importance of the phase state. For several cases, separation of solutes into different subphases or partial precipitation have been observed for model mixtures [Ciobanu et al., 2009]. Internal phase state issues of particles are strongly linked to important questions in atmospheric chemistry. For example, in aerosol chemistry reactive transformations of aerosol constituents by gas phase oxidants depend significantly on the microenvironment (e.g., solid / liquid) they are contained in [Hearn and Smith, 2007]. The morphology of individual particles is also relevant, as their optical properties depend on the spatial distribution and the size of individual scatterers or absorbers within an individual particle [Kocifaj et al., 2006]. For instance, for the system H₂SO₄/H₂O/NH₃, Colberg et al. [Colberg et al., 2004] found evidence for complex morphologies of liquid phases (ammonium bisulfate) embedded in crystalline (letovicite and ammonium sulfate) within a system of pores or grain boundaries. Mikhailov et al. [Mikhailov et al., 2004] found in their bovine serum albumin - NaCl/NH₄NO₃ mixtures evidence for formation of porous agglomerates. However, particle morphology was also found to influence the water uptake behavior of single particles [Mifflin et al., 2009].

Therefore spatially resolved microchemical information for ambient atmospheric particles and model systems as a function of humidity is needed. Some information about internal particle structure has so far been inferred indirectly from kinetic effects of particle growth with increasing humidity in hygroscopicity tandem differential mobility analyzer (HTDMA) measurements for submicron particles [Sjogren et al., 2007] or more directly from scattering experiments with particles in traps such as an electrodynamic balance (EDB) for particles of 10 µm and larger [Colberg et al., 2004]. Such experiments are routinely used to measure water uptake and are therefore interesting for concomitant morphology information. EDB experiments in addition provide options for microscopy and spectroscopy and therefore chemical sensitivity. Given the size range of atmospheric particles, methods with submicron resolution using electrons and x-rays are favorable, and they can be combined with absorption or emission spectroscopy to obtain local chemical information.

Synchrotron based x-ray absorption spectroscopy is highly element specific and, the soft x-ray regime through its near edge fine structure (NEXAFS) provides excellent opportunities to investigate the chemistry of oxygen and carbon in environmental samples. By exciting a core electron of a molecule into an unoccupied molecular orbital (i.e. fine structure at a specific absorption edge) it is possible to distinguish different chemical functional groups in the absorption spectrum. Previous studies showed that the chemical sensitivity of NEXAFS spectroscopy in combination with a microfocus x-ray beam in a
scanning x-ray transmission microscope is a powerful tool to study chemically resolved microstructure of single atmospheric particles. For example, using NEXAFS, Russell et al. [Russell et al., 2002] could map organic functionalities in organic aerosols, which exhibit complex, spatially inhomogeneous mixtures of R(C=O)R, R(CHₙ)R′ and R(C=O)OH. However, experiments with samples in equilibrium with water vapor have not been published so far. Though, scanning transmission x-ray microscopy (STXM) has been performed in wet environmental samples before [Neuhausler et al., 2000] and in a reaction cell for an in situ catalysis study [de Smit et al., 2008]. The combination of single particle analysis with STXM, which is restricted to a few facilities worldwide that offers limited access only, exhibits the drawback that only a limited amount of particles can be studied. Statistically representative studies are still scarce.

Only few studies have been published so far, in which morphological changes in submicrometer sized individual aerosol particles were imaged during water uptake using other high resolution microscopic methods such as transmission electron microscopy (TEM) [Wise et al., 2005]. For example, Wise et al. show water uptake/release experiments with different salt compounds in an environmental TEM (ETEM) by mapping size and shape changes during deliquescence and efflorescence of the individual particles at different RH. Measurements using ETEM provide very good information on the morphology due to the favorable resolution of a few nm and enable also to study deliquescence and efflorescence of individual particles. Spatially resolved spectroscopic information is available using electron energy loss spectroscopy (EELS) but not under high pressure, i.e., wet conditions and due to its worse energetic resolution detailed functional group analysis is far poorer than in NEXAFS spectroscopy [Hitchcock et al., 2008]. Therefore, in spite of lower spatial resolution and typically less available beamtime, STXM provides valuable and novel insight into morphology and phase state of atmospheric particles.

Here, STXM was applied to monitor water uptake in single micrometer sized particles and show the capability of the scanning x-ray microscope to address morphological issues during water uptake onto individual particles. To study the water uptake in these particles a special microreactor was used, which allowed to perform microscopic and spectroscopic studies of water uptake and release processes in situ. The goal was to monitor size/shape/morphology changes using the high spatial resolution of STXM and changes in functionalities using NEXAFS of submicrometer sized particles during exposure to humidity in the microreactor.

Ammonium sulfate was chosen as a reference system because of its relevance in the atmosphere and because its properties during water uptake/release are well known. Ammonium sulfate exhibits a hysteresis behavior during uptake and release of water: solid ammonium sulfate transforms into its saturated solution (deliquescence) once the humidity reaches the so-called deliquescence relative humidity (DRH), which is the water vapor pressure above the saturated solution. If exposed to lower humidity,
the salt in the saturated solution does not crystallize but forms a supersaturated solution down to the so called efflorescence humidity (ERH), where recrystallization (efflorescence) is observed. In salts, this efflorescence point may be significantly below the deliquescence humidity. The deliquescence of ammonium sulfate occurs at about 80 % RH, whereas the efflorescence takes place at about 40 % RH [Sjogren et al., 2007]. In this study the microreactor was used to adjust the RH in order to observe water uptake and release in individual aerosol particles. Therefore, this simple reference system also provides novel spectroscopic information for the supersaturated solutions not available easily otherwise.

An adipic acid/ammonium sulfate mixture was chosen to study morphological effects. Such dicarboxylic acids have been identified in ambient aerosol particles whereby also adipic acid was found to be present in atmospheric aerosols [Ray and McDow, 2005]. The adipic acid is known to be a poorly soluble organic compound in water [Rozaini and Brimblecombe, 2009]. The hygroscopic properties of the mixture with ammonium sulfate were already investigated using HTDMA/TDMA and EDB [Sjogren et al., 2007, Hameri et al., 2002]. These studies indicated formation of two phases in the particles consisting of solid adipic acid and aqueous ammonium sulfate. From kinetic effects it was suspected that the morphology of the two phases may be important.

Using STXM, we tried to clarify the suspected morphology changes in mixed ammonium sulfate/adipic acid particles under the influence of humidity in situ.

### 3.3 Experimental

#### 3.3.1 Sample Preparation

Aerosol particles were generated with a home built ultrasonic nebulizer using N$_2$(>99.9 %) as carrier gas with either a 1 wt % ammonium sulfate solution or a solution of 0.4 wt % adipic acid and 0.13 wt % ammonium sulfate. This aerosol generation method is well established and widely used in aerosol science to generate proxies of atmospheric particles with well defined size distribution and chemical composition [Sjogren et al., 2007]. The substances were purchased from Sigma-Aldrich (Sigma-Aldrich, Basel, CH) and were not purified further. Both solutions were prepared with deionized water (18 MΩ·cm, MilliQ). After nebulizing the solution, the resulting droplets were passed through a silica gel dryer, so that the initial solution droplets dried completely leaving submicron sized dry salt residues as an aerosol. The aerosol was then passed through a Kr-85 source, where charge equilibrium was established. The size distribution of the particles was simultaneously measured by SMPS (scanning mobility particle sizer) consisting of a DMA (differential mobility analyzer) and a CPC (condensation particle counter). The dry particles in the remainder of the flow were deposited electrostatically (0.8
kV) using a corona charger on a silicon nitride membrane window (Silson Ltd., Northampton, UK). The membrane was previously glued with wax onto a small sample holder of the microreactor (see below). The resulting aerosol particles were internally mixed particles (see below). The mode of the number size distribution of the particles was measured to be 400-500 nm, large enough to map morphological changes within the particles during water uptake and release. Special attention was paid that spectra of the particles were not affected by overabsorption (OD > 1.2).

For comparison, bulk samples of ammonium sulfate and adipic acid were prepared. For the bulk sample about 2 g/l of ammonium sulfate and about 0.5 g/l adipic acid was dissolved in MilliQ water and a drop was directly put on the Si$_3$N$_4$ window and dried. During the measurements the sample locations were chosen carefully so that the OD values did not exceed 1.2.

The microreactor with the collected aerosol particles was placed into the microscope maintained under vacuum while keeping the pressure at 150 mbar within the reactor, see below. The temperature of the microreactor was set to 20°C. Bulk samples were measured at atmospheric pressure under He.

### 3.3.2 Scanning Transmission X-ray Microscope

The experiments were performed at the PolLux beamline [Raabe et al., 2008] of the Swiss light source (SLS) at Paul Scherrer Institut (PSI), Switzerland. This synchrotron radiation source operates at a beam energy of 2.4 GeV and electron current of 400 mA. The PolLux beamline provides photons in the energy range of 200-1200 eV with a energy resolution ($E/\Delta E$) of about 3000. It is equipped with a scanning transmission x-ray microscope as an end station. A Fresnel zone plate focuses the x-ray beam down to a spot size of around 40 nm on the sample. The intensity of the transmitted x-rays is measured by detecting the photons in a photomultiplier tube (Hamamatsu 647P) placed directly behind the sample. The high-precision-piezo-technique sample stage can be moved in the sample plane to measure absorption at different sample locations and along the beam axis for focusing purposes (Figure 3.1). The energy calibration of the spectra was adjusted by measurement of the known transitions of polystyrene spheres [Dhez et al., 2003].

The Lambert–Beer law ($OD = -\ln(I/I_0)$) was used to obtain the optical density, $OD = d \mu$, where $\mu$ is the mass absorption coefficient, $d$ the thickness of the sample, $I$ the transmitted light intensity across the sample, and $I_0$ the transmitted light intensity across the sample free region.

Different modes to gain spectral and structural information on individual aerosol particles with the STXM were used. These protocols were developed to reduce beam damage until reproducible spectra were obtained. A careful choice of the particles was done in all measurements so that the OD values did not exceed 1.2.

**Image stack** Image stacks, i.e., a series of images at closed space energy step sizes [Jacobsen et al.,
were used to obtain spectral information on different regions in individual particles. These image stacks were taken in energy steps of 0.2 eV in the range of 284-300 and in 0.5 eV steps in the range of 280-284 and 300-330 eV, respectively. At the oxygen edge, step sizes were used of 0.1 eV from 532-550 eV and 0.2 eV from 525-532 and 550-560 eV, respectively. The nitrogen edge was measured in 0.1 eV steps from 395-420 eV and 0.2 eV steps from 390-395 and 420-430 eV, respectively. The dwell time was set to 1 or 2 ms with a spatial resolution of 60-100 nm. Tests on beam damage revealed a loss in intensity of about 20 % at the oxygen edge with these settings. Note also here, that only one stack was taken for one single particle.

Absorption and Chemical Maps

Highest resolution absorption images of the particles with a typical resolution of 35 nm were taken at a few fixed energies (typically most intense peak energies observed in the NEXAFS spectra). The images measured at energies lower than the absorption edge of an element at 280 eV (carbon) and 520 eV (oxygen) were used for background subtraction. Before the background was subtracted, chemical maps were first converted into optical density maps. Such maps were recorded at different relative humidities in the microreactor (see next section) and were then used to track changes in absorption at the specified energy within individual particles as a function of increasing or decreasing humidity.

The results shown from ammonium sulfate/adipic acid particles were measured with the initial setup of the PolLux beamline. At this point the light was not perfectly monochromatic. Some higher order light originating from the plane grating monochromator could not be filtered out. The amount of this light is estimated to be about 20 % second and 10 % third order at 300 eV. At the oxygen edge this contribution is lower. The presence of this unwanted light reduced the contrast of the images, but did not change the observed structures. To monitor the water uptake in these mixed particles, we rather use spectroscopic features. The ammonium sulfate particles were measured after upgrade of the beamline with a higher order suppressor. The stack alignments and the linescan analysis were done using aXis2000 [Hitchcock, 2006].

3.3.3 The microreactor

The microreactor will be just briefly introduced here. A detailed description of the microreactor has been given elsewhere [Huthwelker et al., 2010]. The design of the microreactor takes into account the strict spatial constraints given by the PolLux microscope (see Figure 3.1) and relies on concepts similar to the chamber used by Drake et al. [Drake et al., 2004]. The microreactor can be mounted on the high-precision piezoelectric stage of the microscope. It consists of two parts: One part comprises of the gas flow inlet and outlet and is covered by one 1 x 1 mm square silicon nitride membrane in a 5 x 5 mm square silicon supporting frame (wafer). The second part is a small sample holder on which the
second, front wafer (window size of 0.5 mm) can be fixed with wax (crystal bond, SPI suppliers, West Chester, USA). The aerosol or bulk samples are deposited on this second wafer as described above. Afterwards, the sample holder can be screwed onto the first device. Combining these two parts gives an isolated chamber with a gas inlet and outlet with the two parallel Si₃N₄ windows serving as windows for the x-rays. The two windows, each 50 nm thick, are about 300 µm apart from each other. Temperature control is also established with the microreactor. While cooling the reactor with a copper wire attached to a liquid nitrogen dewar a heater allowed adjusting the temperature of the reactor to the required temperature.

A small flow (20-50 ml/min) of helium at 150 mbar was passing through the microreactor. A variable fraction of this flow was passed through a saturator, where it equilibrated with the water vapor pressure at room temperature. This allowed adjusting the RH in the microreactor. The RH was measured using capacity sensors operated at room temperature at the exit line leaving the microscope chamber, and a thermocouple mounted at the microreactor itself was used to correct the relative humidity for the precise temperature in the microreactor using 'humicalc' from Michell Instruments (Cambridgeshire, UK), which is based on the formula presented by Sonntag [Seinfeld and Pandis, 1997]. The accuracy of the RH measurements is about ± 2 %. The microreactor itself is tight and can bear 0.2 bar overpressure. The pressure in the microreactor and the gas flows are controlled by a LABVIEW program.

Figure 3.1: Schematic showing the microreactor placed in the PolLux microscope, components as the order sorting aperture (OSA) are shown. Colored in rose is the sample holder with the Si₃N₄ wafer on which the aerosol particles are deposited.

### 3.4 Results and discussion

First, we discuss the investigation on water uptake and release from pure ammonium sulfate aerosol particles deposited in the microreactor. The main objective of this part was to obtain spectroscopic data for pure ammonium sulfate, its subsaturated and supersaturated solutions, and to use the spec-
trosopic features to describe water uptake of ammonium sulfate particles as a test case. In a second step, the morphology was studied of the particles consisting of a mixture of ammonium sulfate and adipic acid.

3.4.1 Water uptake on individual ammonium sulfate particles

**Deliquescence of Ammonium Sulfate Particles** In Figure 3.2 STXM absorption images (normalized to $I_0$) are shown taken at 560 eV from the same ammonium sulfate particle at 0 %, 81 %, 86 % and 65 % (during drying) RH. The change of the particle size due to the uptake of water is apparent, especially between 0 and 81 %, whereby the latter is one percent higher than the well-known deliquescence point of ammonium sulfate. During drying from 80 to 60 % the absorption intensity reduces indicating a substantial loss of water.

![Figure 3.2: Absorption maps of an individual ammonium sulfate particle at four different RH (0 %, 81 %, 86 % and 65 % during drying) measured at 560 eV.](image)

The measured O K-edge spectra of ammonium sulfate are depicted in Figure 3.3, Figure 3.4 and in more detail in Figure 3.5, along with a bulk water spectrum reported earlier by Tzvetkov et al [Tzvetkov et al., 2008]. All spectra were pre-edge subtracted and normalized to the highest absorption peak to enable a direct comparison of the spectroscopic features among the individual spectra. Linescans and stacks were applied only once for one particle to avoid effects due to beam damage, which appeared as decrease in intensity. I.e., one spectrum corresponds to one particle, strictly following the protocols described in the experimental section. To make sure, that no larger beam damage occurred during the measurements, additional spectra at the nitrogen edge were measured. One spectrum is shown in Figure 3.6 from a dry ammonium sulfate particle. The main absorption is found at 406 eV, which is in agreement with other reports [Leinweber et al., 2007]. Nitrogen spectra were also taken from the supersaturated ammonium sulfate solution and its diluted solution. All spectra showed the main absorption from the $1s \rightarrow \sigma^*$ transition at 406 eV. However, no absorption was observed at 400.8 eV, the $1s \rightarrow \pi^*$ of N$_2$, in any of the cases even after repeated exposure of a single particle to the beam. Since this absorption is used as marker for beam damage [Leinweber et al., 2007], no large beam damage is expected during the measurements also at the oxygen edge.
The spectra from individual particles are noisier compared to spectra taken from bulk samples because of the small dwell times and because of the low absorption by the optically thin, small particles as compared to bulk measurements.

The discussion of the different spectra focuses on four main regions of interest. These are 535.1-536.1 eV (region A or pre-edge [Wernet et al., 2004]), 536.9-538.1 eV (region B, main-edge), 539-542 eV (region C, post-edge) and 546-548 eV (region D). Figure 3.3 shows spectra of individual particles during water uptake at 22.5 %, 49 % and 88 % RH and for comparison a spectrum from bulk ammonium sulfate. The spectrum measured at 22.5 % RH can be considered as a pure ammonium sulfate reference spectrum, as ammonium sulfate does not take up water under such dry conditions. It is consistent with the bulk ammonium sulfate spectrum, which was measured under helium. Consistent with this, spectroscopic features of water in the spectrum are absent. This spectrum exhibits the main absorption at 537.5 eV. This agrees with the sulfate main edge absorption reported by Todd et al. [Todd and Sherman, 2003; Todd et al., 2003] for CoSO₄ and Fe₂(SO₄)₃, which was found at 537.6 eV and with the CeSO₄ spectrum measured by Rodriguez et al. [Rodriguez et al., 1999], where the main absorption of sulfate was reported to be at 538 eV. A slightly different spectrum of ammonium sulfate with the main absorption edge at 536 eV was measured by Bresch et al. [Bresch, 2007] using a free nanoparticle beam. The main absorption peak was assigned to the transition from O(1s) to an S-O antibonding orbital [Todd et al., 2003]. The absorption peak shows a shoulder at 536.8 eV reproducibly found in all spectra of non-deliquesced ammonium sulfate. One more peak was observed at about 547 eV (region D), similar to FeSO₄, CoSO₄ [Todd and Sherman, 2003; Todd et al., 2003] and Ce₂(SO₄)₃ at about 546 eV [Rodriguez et al., 1999], which might be related to Rydberg transitions due to its broadened shape. A very weak absorption is found in few of the spectra of individual ammonium sulfate particles at 532 eV. This peak was not observed in the bulk ammonium sulfate spectrum. In other comparable cases, this absorption has been attributed to organic contaminations and would then represent a 1s to \( \pi^* \) transition [Ishii and Hitchcock, 1988]. If a peak at this energy had appeared in spectra of different dry particles the intensity was quite variable, as might be expected for contaminations in the sample [Tzvetkov et al., 2008, Bluhm et al., 2002]. The contamination is possibly introduced during generation of the aerosol particles. The compounds absorbing at 532 eV in the ammonium sulfate spectra might also have influenced the shape of the main absorption edge, which can cause problems in the interpretation of the spectra. This weak absorption was also observed at 532 eV in some of the wet ammonium sulfate spectra (≥ 80 % RH). However, spectra were also taken at the carbon edge in various particles, but no absorption could be measured. The spectrum at 49 % RH is very similar to the spectrum at 22.5 % RH as well as to the spectrum measured at 65 % RH. At this point ammonium sulfate still did not reach the deliquescence point. The spectrum at 88 % RH, after deliquescence of ammonium sulfate, shows already particular changes in the absorption features characteristic of the water transitions contributing
to the spectrum. The x-ray absorption spectrum of pure water (also shown in Figure 4 and 5) is already well known but still under debate with respect to the exact interpretation of individual features [Wernet et al., 2004, Smith et al., 2004]. Avoiding such detailed interpretation, we just note the general features in the spectrum with a shoulder at 535.5 eV commonly assigned to free OH (not hydrogen bonded), a main edge at 537 to 538 eV, and a post-edge feature at 540 to 541 eV. The most obvious change of the ammonium sulfate spectrum at 88 % RH as compared to the dry ammonium sulfate spectrum is the increased shoulder at about 541 eV (Figure 3.3, region C). The absorption at 536.8 eV observed in the dry ammonium sulfate spectra disappeared, while a shoulder at 535.5 eV similar to that in water appeared. Furthermore, a small shift of the main edge to resemble that of water was observed. The pre-edge feature is slightly higher than the feature of pure water similar to the spectra reported by Cappa et al. [Cappa et al., 2005] for up to 4M NaCl solutions. Also the broad peak at 547 eV (region D) disappears from the spectrum as the water transitions start to dominate the spectrum. At 88 % the molecular composition of the solution is expected to be \((\text{NH}_4)_2\text{SO}_4 + 17 \text{H}_2\text{O}\). This relation was calculated from the change in the particle mass observed in EDB experiments [Xu et al., 1998].

Figure 3.3: NEXAFS spectra of single ammonium sulfate particles during exposure of the particles to increasing humidity (hydration); a) bulk spectrum of ammonium sulfate, spectrum b) is a spectrum of a single particle at 22.5 %, c) at 49 %, d) at 88 % RH.

Efflorescence of Ammonium Sulfate Particles Figure 3.4 shows three spectra measured during water release starting with the spectrum measured at 83 % RH showing the same absorption features as described for the spectrum at 88 % RH. As in the previously discussed case at 88 % RH (see Figure 3.3), the similarity to the one of bulk water is apparent from the shoulder at 535.5 eV and the absorption in region C. During water release, when a supersaturated solution forms, interesting changes in the spec-
tra can be observed. Note that x-ray absorption spectra from supersaturated solutions are not available in the literature to compare with. Figure 3.4 illustrates a spectrum measured at 64 % RH. The shoulder at 535.5 eV in region A has decreased substantially compared to the spectrum measured at 83 % RH, while the absorption at 536.8 eV observed in dry ammonium sulfate has not become apparent. On the other hand, it still contains a substantial share of the water feature around 541 eV and the wider and slightly shifted maximum at 538 eV (Figure 3.5). The spectrum of the supersaturated solution cannot be completely explained by linear combination of the water and the ammonium sulfate spectra, see below. The spectrum of ammonium sulfate recorded at 0 % RH, after efflorescence, shows again the typical features of a normal dry spectrum of ammonium sulfate with the shoulder at 536.8 eV and the broad absorption at about 546 eV.

Figure 3.4: NEXAFS spectra of single ammonium sulfate particles exposed to decreasing relative humidities (dehydration). Spectrum a) was measured at 0 %, b) at 64 %, c) 83 % and d) a water spectrum [Tzvetkov et al., 2008].

Figure 3.5 shows a detailed view of the spectra measured at 88 % (Figure 3.3), at 78 % and 66.5 % during dehydration of the ammonium sulfate, at 22.5 % RH (Figure 3.3) and for bulk liquid water. It emphasizes the differences described above between the supersaturated solution of ammonium sulfate, the dry ammonium sulfate spectrum and the water spectrum, respectively. Note that lowering of the RH by few percent to 78 %, just below the deliquescence humidity, reduces the pre-edge at 535.5 eV substantially as discussed for the supersaturated solution measured at 64 %. Region C shows already lowered absorption intensity due to loss of water. Modelling of the spectrum from supersaturated solutions by linear combination of the water and the dry ammonium sulfate spectrum failed. While it worked well for the absorption intensities in the pre-edge and post-edge regions, the energy shift of the main edge from the supersaturated solution at 537 eV could not be reproduced by linear combination of the two spectra. As described above, the spectral
3.4. Results and discussion

**Figure 3.5:** Normalized spectra of water and ammonium sulfate particles at different relative humidities. Blue: water spectrum, light blue: ammonium sulfate at 88 % RH, black: 78 % RH during efflorescence, magenta: 66.5 % RH during efflorescence and in red: 22.5 % RH. The greyish bars mark the regions with the changes.

**Figure 3.6:** Nitrogen spectrum of a dry ammonium sulfate particle

Changes in the pre-edge region due to the water uptake are complex and not necessarily related to the amount of water in the particle, but rather sensitive to the hydrogen bonding environment [Wernet et al., 2004]. The only spectroscopic feature, which was smoothly changing during water release and uptake, was the shoulder at about 541 eV. Therefore, this region was used for a qualitative analysis of the spectra with respect to water uptake. The integrated region from 538 to 545 eV of the normalized spectra was plotted against the adjusted RH, see Figure 3.7. Additionally, a plot was added to the graph to show the oxygen mole fraction of water in the ammonium sulfate solution \( x_{H_2O}/x \) with \( x = \) total of...
moles of oxygen atoms in the mixture) derived from mass growth measurements in EDB experiments, which are also in line with thermodynamic estimates [Xu et al., 1998]. The black squares represent the intensity of the integrated region (538-545 eV) of the dry ammonium sulfate spectra during water uptake, while the red dots represent the corresponding signal during water release. Each data point corresponds to a different particle. Note that the appearance of the humidogram in Figure 3.7 in terms of water mole fraction, which has been used because the oxygen is the available observable, is quite different from the more usual way of plotting it in terms of diameter or mass growth factors, which increases towards infinity for high humidity. The integrals for the dry particles show a certain scatter, although the integral is always lower than that for the (supersaturated) ammonium sulfate solution. This might be related to small contaminations as discussed above. At 80 % RH an increase of the integrated peak intensity can be observed indicating the deliquescence of the ammonium sulfate. Above DRH (80 % RH) the ammonium sulfate continues taking up water consistent with the established humidogram (see also Figure 3.2). When lowering the humidity below the DRH value, the salts do not precipitate from the solution, but rather a hysteresis behavior is observed in the humidogram with its efflorescence point at around 40 % RH, consistent with many other observations in the literature [Sjogren et al., 2007]. Although there is some scatter in the amount of water estimated to be associated with the particle from the spectral analysis, the major features were found to be consistent with the expected behavior during hydration and dehydration. This is in agreement with hygroscopicity measurements found with other methods, such as HTDMA, EDB, and TEM [Sjogren et al., 2007, Wise et al., 2005].

3.4.2 Morphological studies on adipic acid/ammonium sulfate mixtures

A mixture of adipic acid and ammonium sulfate (molar ratio of sulfate to adipic acid is about 0.42) was measured and analyzed at low RH (7 % and 26 %) and at high RH (84 %) at the carbon and oxygen edge using chemical maps and image stacks.

**Carbon edge**  Figure 3.8 shows chemical and absorption maps at the carbon absorption edge of the ammonium sulfate and adipic acid mixture at low and high RH. Figures a-d and e-h each show a series of four images taken at different humidity of one individual particle, respectively. Figure 3.8 a, c, e and g show absorption images at 270 eV. At this energy, below the absorption edge of carbon, also other elements than carbon absorb a finite amount of the light, i.e. at this energy also ammonium sulfate is found to have a distinct absorption intensity due to non-resonant transitions involving valence electrons of N, C, O and S. It can be estimated that dry ammonium sulfate has an about 65 % higher absorption intensity at 270 eV than adipic acid assuming a mass ratio of 1:3 [Henke et al., 1993]. Therefore,
3.4. Results and discussion

Figure 3.7: Integrated spectra intensity between 538-545 eV spectra of single ammonium sulfate particles (one spectrum, i.e., one data point corresponds to one particle) at different RH showing a humidogram similar to those found in the literature. The black squares show the integral during hydration, the red circles represent the measurements during drying. The blue dot represents the integral region of pure water, while the green square shows the integrated peak of bulk ammonium sulfate. The orange star shows the integral of the mixture of adipic acid and ammonium sulfate in the same region (see second part). The dotted lines are the mole fraction of the oxygen atoms of water in ammonium sulfate solution adapted from Xu et al. [Xu et al., 1998].

these images reflect the general contours of the particles with ammonium sulfate as stronger absorber. Figure b, d and f, h show carbon chemical maps measured at 288.5 eV and 289.5 eV, respectively. The color scale in the image represents an absorption scale, dark blue represents high absorption and white no absorption. The red line drawn in Figure 3.8 a indicates the elemental distribution of carbon in the particle, which is shown in Figure 3.8 b. This figure shows a particle measured at 7 % RH at an energy of 288.5 eV, which is known to be the energy of the sharply resolved $\pi^*_{C=O}$ transition (see below). Comparing Figure 3.8 a and b shows the irregular shape of this particle and the heterogeneous distribution of the adipic acid in the particle. All investigated particles showed a slightly different morphology. Note that the history of this particle is formation of a droplet in the nebulizer, drying to a polycrystalline particle and deposition on the sample holder as a dry particle before this experiment. In any of these steps, coagulation could have occurred, which could have resulted in the structure observed, and which is a
Chapter 3. Water uptake in submicron particles

Figure 3.8: Carbon chemical (b, d, f, h) and absorption maps (a, c, e, g) of submicrometer sized particles consisting of adipic acid and ammonium sulfate showing the distribution of adipic acid in the particles. Images a-d show one individual aerosol particle at different RH (a and b at 7 %, c and d at 84 % RH). Images e-h show a second single aerosol particle measured at 26 % RH (e and f) and at 84 % RH (g and h). Particles were measured at 270 eV (a, c, e, g), 288.5 eV (b, d), and 289.5 eV (f, h). Red line in a and e indicates elemental carbon absorption.

common process during the physical evolution of atmospheric particles.

Raising the RH in the microreactor to 84 %, above the deliquescence RH of ammonium sulfate, results in a rearrangement of the carbon as shown in Figure 3.8 d, measured at 288.5 eV. In comparison to Figure 3.8 b the particle becomes larger with a round shape with a strong absorption of the carbon in the center. This chemical map shows a sharp border separating the inner core from the residual part of the particle, which indicates an isolated carbon containing part. For this image, the pre-edge absorption is subtracted, so that it represents absorption by carbon only. Hence, adipic acid remains as a solid structure surrounded by a substance, which was found to be the ammonium sulfate solution (see below), and the two individual carbonaceous structures observed in the dry particle apparently coalesced. The deliquescence of the particle is indicated by the increase of its size (Figure 3.8). Although a strong contrast was found between the carbonaceous inclusion and its surrounding, a small but significant absorption is observed in the residual part of the particle. The solubility of adipic acid in pure water is low, 21 g/l [Rozaini and Brimblecombe, 2009], so that dissolved adipic acid could not significantly contribute to absorption. It is therefore likely that a thicker layer of adipic acid on top or underneath the solution is responsible for absorption there.

A comparative study by Yeung et al. [Yeung et al., 2009] using optical microscopy and Raman spectroscopy shows microscopic images and Raman spectra of 5-20 µm sized ammonium sulfate/adipic acid particles under different RH. In this study a phase separation of deliquesced ammonium sulfate and adipic acid is reported. Their spectra of the ammonium sulfate solution show also features from
adipic acid but this was explained by the bad spatial resolution of the laser.

Figure 3.8 e shows a picture of a second particle measured at 270 eV at 26 % RH. Again, a red line indicates the elemental distribution of carbon as shown in Figure 3.8 f. This figure shows the pure elemental distribution of carbon in the aerosol particle measured at 289.5 eV. Here, one can observe the same situation as observed in Figure 3.8 a: irregular shape with heterogeneous distribution of the adipic acid. Enhancing the RH in the microreactor to 84 % results in a similar structure with an organic core as in Figure 3.8 b.

The carbon spectra confirm the observations of the images in Figure 3.8, although they were taken with less spatial resolution but higher energy resolution to minimize beam damage. At low RH a similar heterogeneous distribution (data not shown) was found as described in Figure 3.8 a, b and e, f, respectively.

Figure 3.9 shows a chemical map of a particle at 84 % RH. The picture was taken at an energy of 288.5 eV. The particle is large (> 1 µm) with a round shape, and the adipic acid again appears as a strong absorber in the middle of the wet particle. The corresponding spectra are shown in Figure 3.10. No normalization was performed to enable direct comparison of the different absorption intensities in the heterogeneous regions A and B of the particles (Figure 3.9).

The spectroscopic features of the adipic acid spectrum can be assigned to the sharply resolved C=O π∗ peak at 288.6 eV, the C-H resonance at 292.9 eV, the C-O σ∗ at 297.7 eV and possibly the C=O σ∗ resonance at about 303 eV. This assignment of the spectrum was adopted from Outka et al. [Outka et al., 1987] assuming that the adipic acid spectrum is the superposition of the NEXAFS features expected for the functional groups in adipic acid [Outka et al., 1987, Ishii and Hitchcock, 1988].

These spectra were extracted from two different sample regions as indicated in Figure 3.12: Region A, the strong absorbing part in the particle, and region B. The spectra show a strong absorption intensity at the carbon edge for region A (the detailed description of the adipic acid spectrum is given below). Although low in intensity, the spectrum of region B shows still all features of an adipic acid absorption spectrum indicating the presence of small amounts of this acid also in the residual part of the particle. This is consistent with the information already retrieved from the chemical maps discussed above, and additionally support the suggestion that absorption in this part of the particle is due to adipic acid, and rather not a contamination species (at least not one other than a carboxylic acid).

**Oxygen edge** Spectra and images were also taken at the oxygen absorption edge. To find absorption features of adipic acid and ammonium sulfate, which allow to distinguish between these compounds at the oxygen edge a bulk sample was prepared of pure adipic acid. The spectrum was measured in the linescan mode in steps of 0.1 eV from 525-560 eV (Figure 3.11). The assignment of the absorption features was adopted from Ishii et al. [Ishii and Hitchcock, 1988] taking propanoic acid measured in the gas phase as reference. The sample was prepared by dissolving the adipic acid in MilliQ water, drying
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Figure 3.9: Carbon chemical map (pre-edge subtracted) of a particle consisting of ammonium sulfate and adipic acid measured at 288.5 eV at 84 % RH. Below is shown a cut through the image to illustrate the absorption intensity in the middle of the particle. The spectra related to this picture are found in Figure 3.10.

Figure 3.10: Carbon K-edge spectra of adipic acid obtained from different regions (region A and B) in the aerosol particle, Figure 3.9.

on the sample holder, which resulted in a dendritic crystalline form of adipic acid. This spectrum was also compared with the spectra reported by Hasselstroem et al. [Hasselström et al., 1998] who measured NEXAFS spectra at different incident photon angles from acetate, formate and glycine condensed on Cu. The adipic acid spectrum exhibits the same features as the formate and ac-
etate spectrum on the Cu [110] surface, with the double peak at 532.5 eV, the single peak at 535.5 eV and the broad absorption bands at above 540 eV. As discussed in conjunction with Figure 3.3 and 3.4, the spectra of ammonium sulfate do not exhibit an absorption at 532.5 eV. Hence, the peak at 532.5 eV distinguishes the organic from the inorganic compound in the mixture in the oxygen absorption region.

Figure 3.12 shows STXM images of a particle measured at 84 % RH at three different energies. The left panel shows the particle at 532.5 eV. It is apparent that the organic formed an inclusion-like shape in the particle, which is consistent with the observation made at the carbon edge. Furthermore, the adipic acid is not solely concentrated in the core of the particle but also a small absorption appears near the border of the particle. A complimentary structure can be observed in the image measured 538 eV. At this energy ammonium sulfate and water are the strongest absorbers in the mixture. The ammonium sulfate solution shows a ring-like structure around the organic. The image in the right panel in Figure 3.12 was measured at 541 eV and shows the same profile. This energy is mainly attributed to the absorption of water (see Figure 3.3 for an ammonium sulfate spectrum). Obviously, less absorption was measured in the organic part indicating a lower amount of water than in other regions and suggests that adipic acid remained undissolved, even though the amount of solution seems still significant at the location of the maximum amount of adipic acid. This is further substantiated by associated spectra shown in Figure 3.13. In Figure 3.13 a) the spectrum of a separate dry particle is shown with a pronounced peak at 532.5 eV indicating the presence of adipic acid in the particle. In Figure 3.13, plots b) and c) show spectra from the particle illustrated in Figure 3.12, whereby spectrum b) is extracted from region C in Figure 3.12 and spectrum c) from region D. Compared to the spectrum of the dry mixture in Figure 3.13 a), various changes in the absorption intensities are apparent consistent with the water uptake in the particle. The shoulder at 541 eV raised and the absorption at 535.5 eV is increased too as described for the ammonium sulfate solution. Also the violet shift of the main edge absorption

![Image](image.png)

**Figure 3.11:** Oxygen K-edge spectra of adipic acid
intensity from 537.5 to 538 eV can be observed again, which is attributed mainly to the dominant presence of water once a solution forms. Note that also the spectrum b) taken at the location of adipic acid shows the features identified as deliquesced sulfate solution before, and also the absorption intensity at 532.5 eV, which is attributed to the adipic acid, decreased compared to the intensity at the main edge. The main edge is clearly at 538 eV characteristic of the sulfate solution rather than 540 eV for adipic acid. Therefore, in the region, where most of the adipic acid resided under wet conditions, the sulfate solution was substantially contributing to absorption. An unknown feature evolves at about 542.5 eV. Unfortunately, we are not able to assign this absorption, because it does not appear in any of the reference spectra of water, dry adipic acid or dry/wet ammonium sulfate. It might be that the $\sigma_{\text{C-O}}$ transition contributes more to the mixed spectra than expected from the reference spectrum shown in Figure 3.11 leading to a larger separation of the water feature around 542 eV from the peak closer to the main edge. Besides these explanations, also a solvent effect could explain this dip as seen in water and ice [Bluhm et al., 2002, Myneni et al., 2002]. The presence of some higher harmonic light could have affected the spectra, hence, we refrain from a further analysis here.

The intensity for the spectral region from 538-545 eV was integrated, assuming that this region is still dominated by water absorption, for the normalized spectrum c). The value of this integral is included in Figure 3.7 depicted as an orange star showing that the water content in this solution is consistent with that derived from the pure ammonium sulfate particles.

The comparison of the indirect conclusions drawn by Sjogren et al. [Sjogren et al., 2007] from HT-DMA experiments with our data shows a certain consistency. Their studies indicate that adipic acid remains solid up to 99.9 % RH even in mixtures with ammonium sulfate, which is in contrast to studies with other organic compounds like maleic acid, where full deliquescence of the particles was observed [Brooks et al., 2003, Braban and Abbatt, 2004]. Hence, adipic acid was regarded as an inert aerosol component suspected to form solid structures in the ammonium sulfate solution. Furthermore, they assume that the morphology of the mixture during water uptake plays a crucial role in these processes. Arguing that the *inverse Kelvin effect* influences the irregular water uptake (compared
3.4. Results and discussion

Figure 3.13: a) is the absorption spectrum of an adipic acid/ammonium sulfate particle at 26 % RH. b) is the spectrum from a particle at 82 % RH from region C in Figure 3.12. c) shows the spectrum of region D in Figure 3.12. The spectra are divided into three parts where the highest contribution of the different absorption intensity of the compounds (AA, AS and water) is expected. Note that particle of spectrum a) does not correspond to the particle of spectra b) and c).

to the Zdanovskii Stokes Robinson (ZSR) approach [Stokes and Robinson, 1966]) they suggested the existence of a vein and pore system in the particle, which is decisive for the water uptake in the mixed particles. They conclude from SEM images that the dry particles are nanocrystals with irregular shapes consisting of cracks, pores and vein systems with diameters of 20-100 nm. For wet particles they suggested that these veins and pores are filled with aqueous ammonium sulfate due to diffusion of the water molecules into these veins and pores influenced by the inverse Kelvin effect.

Our results show that at low RH (7 % and 26 %) a heterogeneous mixture of the two compounds exists with an agglomerated structure. The detailed history e.g., the drying rate of the nebulized droplets, may determine the structure of the resulting particle, as observed for letovicite particles [Rosenoern et al., 2008]. The suspected morphology of pores and veins at the low nanometer scale can not be assessed, due to insufficient resolution of the microscope. At least, in regions with a significant share of adipic acid, the ammonium sulfate still substantially contributed to the spectrum (Figure 3.13), not contradicting the idea of ammonium sulfate in porous adipic acid. However, we cannot conclusively distinguish such a case from a layer of sulfate solution residing on top of a pure adipic acid phase. On the other hand, inhomogeneities are also observed on the larger scale of 0.2 \( \mu \)m, eventually due to excess of ammonium sulfate not contained in adipic acid. At high RH (> 80 %), Sjogren et al. assume adipic acid to be an inert constituent in the aerosol which does not take up water. This is consistent with our measurements which indicated a solid adipic acid core, a conclusion based on the image stacks obtained from the particles at different RH. The fact that ammonium sulfate was deliquesced, is
clearly evident from the spectra of the mixture and from the apparent growth of the particle. Surprising is the fact that adipic acid was more often found in the center of the particle, because the adipic acid was expected to be at the border of the particle as observed by Yeung et al. [Yeung et al., 2009]. Apart from a significant difference in the size of the ammonium sulfate particle, this might be due to the presence of the Si$_3$N$_4$ substrate, which could play a role in the way the ammonium sulfate solution spreads. While an ammonium sulfate solution did not seem to wet the wafer very well, dissolved adipic acid could be important in lowering the surface tension of the mixed solution [Booth et al., 2009], and so causing the solution to spread around the solid adipic acid, an effect found with other organic substances [Shulman et al., 1996]. Especially, if adipic acid would contain ammonium sulfate in its pores, consistent with our observations with proper reservations as explained above, such concentric spreading might be supported. Therefore, extrapolation of the microstructure of the particles on the substrate to those suspended in the gas should be done with care.

3.4.3 Conclusions

In this paper, first results were presented of investigations into hygroscopic properties of individual submicron particles using NEXAFS spectroscopy combined with the high spatial resolution of the STXM. The novelty is that this has been possible with submicron particles, while other single particle studies combining chemical and hygroscopicity investigations have used much larger particle sizes. The measurements were performed in a microreactor constructed for this purpose. As reference, oxygen K-edge x-ray absorption spectra were measured of: i. the dry ammonium sulfate; ii. deliquesced ammonium sulfate and iii. the supersaturated solutions of ammonium sulfate with features distinct from the other two cases. The spectra of deliquesced and supersaturated ammonium sulfate solutions were not reported before in the literature. One major post-edge feature (538-545 eV) representing liquid water was used to construct a humidogram, which appeared to be consistent with the water concentration in the solution obtained with other methods. Therefore, the possibility was established to use the combination of NEXAFS and STXM to map water uptake in individual submicrometer sized particles based on spectroscopic features.

Further, microscopic images and spectra of particles were presented consisting of a mixture of adipic acid and ammonium sulfate to study the morphology of these mixed particles as function of RH using spectroscopic features at both the carbon and the oxygen edge. Under both, dry and wet conditions, adipic acid and ammonium sulfate were heterogeneously distributed. Under wet conditions, the organic and inorganic patches coalesced into a phase dominated by the ammonium sulfate solution with only minor amounts of adipic acid. This liquid phase coexisted with a structure containing likely undissolved adipic acid with ammonium sulfate solution either on top or in the interior, the microstructure
of which could not be resolved. Therefore, this study sheds additional light on the microstructure of organic / inorganic mixtures under changing humidity. For instance, the optical properties and their nucleation behavior [Schlenker et al., 2004] of such particles will strongly depend on such microstructure, respectively.

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Bibliography


Chapter 4

Humidity driven nanoscale chemical separation in complex organic matter

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4.1 Abstract

Humic like substances represent an important fraction of particulate organic matter in the atmosphere. Understanding their water uptake behavior and the associated evolution of their morphology supports the assessment of their ability to act as cloud condensation nuclei properties as well as their behavior as scatterer of light. The water uptake properties of Suwannee River Fulvic Acid, as proxy for HULIS, and tannic acid were investigated using x-ray absorption spectroscopy in combination with a scanning transmission x-ray microscope. For both compounds continuous water uptake was observed, whereby in bulk fulvic acid phase separation occurred, resulting in an inhomogeneous mixture. Within the inhomogeneous mixture, different regions in the samples with different amounts of water uptake could be differentiated based on spectral signatures in near-edge X-ray absorption fine structure (NEXAFS) spectra, thus based on carbon functional group signatures. Carboxyl-poor compounds were found to be separated from carboxyl-rich compounds when water was taken up. This main differentiation into fractions with high/low water uptake ability could be further refined using phenols, aromatic groups, O-alkylic groups as well as carbonyl functional groups.

4.2 Introduction

Organic compounds play a crucial role in atmospheric chemistry. They can contribute to atmospheric aerosols up to almost 90 wt% [Kanakidou et al., 2005, Jacobson et al., 2000] whereby a substantial part is water soluble [Saxena and Hildemann, 1996, Decesari et al., 2000]. The ability to take up water is an important factor for their ability to act as cloud condensation nuclei (CCN) [Dinar et al., 2006], in heterogeneous processes [Hallquist et al., 2003], but also in the scattering of the aerosol particles in the atmosphere [McFiggans et al., 2006, Haywood and Boucher, 2000, Andreae and Gelencser, 2006]. A significant fraction of these organic substances has also been referred to as Humic Like Substances (HULIS) [Stevenson, 1994], due to their comparable separation behavior on analytical exchange columns as observed for humic substances. In mass spectrometric analysis, these species typically show up at m/z above 300 [Dron et al., 2010]. Such macromolecules were also found in extracts in air masses affected by biomass burning events. The atmospheric HULIS are a complex mixture of organic compounds comprising aromatic structures, carboxylic acids, hydroxyl- or carbonyl-compounds [Salma et al., 2010, Havers et al., 1998], which depends strongly on their origin, age and location. Thus different properties of atmospheric HULIS are expected. Due to their similarity to humic substances in some aspects [Graber and Rudich, 2006], humic or fulvic acids have been used as proxy compounds for HULIS. The fulvic acids, produced by biodegradation, are extracted from soil and other solid phase sources using strong bases. Such natural organic matter (NOM) was shown to exhibit
4.3. Experimental Section

structural inhomogeneities [Schumacher et al., 2005, Lehmann et al., 2008, Kinyangi et al., 2006, Diallo et al., 2005]. The small inhomogeneities, which can occur down to nanometer scales, vary with their chemical structure.

Suwannee River Fulvic Acid (SRFA) was chosen for the investigation of the morphology upon water uptake, since this compound class of well defined origin has been used in numerous other studies of related context, e.g. [Fuzzi et al., 2001, Brooks et al., 2004, Chan and Chan, 2003, Kiss et al., 2005, Dinar et al., 2006, Dinar et al., 2007]. Since the composition of this mixture and its comparability to atmospheric HULIS is still under discussion, an additional chemically well defined compound was chosen for the present investigations. Cowen et al. introduced tannic acid and its photo-degradation products as proxy compound for HULIS [Cowen and Al-Abadleh, 2009]. Tannic acid is a multifunctional molecule that contains a sugar ring and polyphenols connected by ester groups, see Figure 4.1. Compared to humic substances tannic acid is more oxygenated with a higher degree of unsaturation and weaker acidity [Cowen and Al-Abadleh, 2009]. Tannic acid belongs to the family of also naturally occurring tannins.

NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy in combination with a scanning x-ray transmission microscope (STXM) was used to investigate water uptake in SRFA and tannic acid. The excitation of a core electron of a molecule or atom into unoccupied orbitals results in absorption resonances, which appear around the ionization threshold (i.e. absorption edge). In complex mixtures, these resonances can be used to characterize the mixture in terms of chemical functional groups [Stöhr, 1992]. The combination of this technique with an x-ray microscope gives the possibility to map the functional groups with high spatial resolution of 40 nm in atmospheric particles [Russell et al., 2002, Maria et al., 2004, Schumacher et al., 2005, Lehmann et al., 2008]. The advantage of the x-ray studies measured within the so-called water window (x-ray photon energy between the carbon- and oxygen K-edges) is that x-rays can penetrate to a certain extent aqueous samples, which enables investigations of hydrated samples [Hitchcock et al., 2008]. To study in situ water uptake in these compounds a custom microreactor was used. We monitored changes in size, shape and microstructure using STXM in combination with NEXAFS in submicrometer sized particles and droplet residues during exposure to humidity in the microreactor. Here, first studies on quantitative water uptake in SRFA and tannic acid are presented in relation to their chemical functionality.

4.3 Experimental Section

**STXM-NEXAFS** The experiments were performed at the PolLux beam line [Raabe et al., 2008] of the Swiss light source (SLS) at Paul Scherrer Institut (PSI), Switzerland. Photons in the range of 200-1200 eV with an energy resolution ($\Delta E/E$) of 3000 are provided. The end station is equipped with an scanning
transmission x-ray microscope (STXM). The Fresnel zone plate, the focussing element of the microscope, enables to perform microscopy with a spatial resolution of 40 nm for the present experiments. The well known transitions of polystyrene spheres [Dhez et al., 2003] (Agar Scientific, England) were used for energy calibration. The Lambert–Beer law \( \text{OD}=\ln(I/I_0) \) was used to obtain the optical density, with \( \text{OD}=d \cdot \mu \), with \( \mu \) being the linear attenuation coefficient and \( d \) the sample thickness. Image stacks [Jacobsen et al., 2000], i.e. sequences of images recorded at close energy step sizes, were used to obtain spatially resolved spectroscopic information. The energy step sizes were chosen to be 0.2 eV between 530 and 550 eV and 0.5 eV for 520-530 eV and 545-560 eV at the oxygen edge, and 0.15 eV for 284-293 eV and 0.3 eV for 280-284 eV and 293-320 eV. In the evaluation only regions were considered, where the OD did not exceed 1.2. Note, that the spectra were recorded only once per investigated region to reduce beam damage.

Images with highest spatial resolution were measured at few selected energies. These images were converted into absorption maps, by normalizing the images using the Lambert-Beer law. Here, \( I_0 \) was determined from a sample free region in the image stacks. Chemical maps were obtained by subtracting the pre-edge absorption from the absorption maps. The water map was calculated using

\[
\text{water\_column} \approx \frac{\text{OD}_{550} - \text{OD}_{532} \cdot \mu_{\text{fulvic}_{532}}}{\mu_{\text{H}_2\text{O}}} \cdot \mu_{\text{H}_2\text{O}}
\]

with \( \text{OD}_{532} = d_{\text{fulvic}_{532}} \cdot \mu_{\text{fulvic}_{532}} \) for the dry fulvic acid and \( \text{OD}_{550} = d_{\text{fulvic}_{550}} \cdot \mu_{\text{fulvic}_{550}} + d_{\text{H}_2\text{O}} \cdot \mu_{\text{H}_2\text{O}} \) for the humidified fulvic acid. \( \mu_{\text{fulvic}_{550}} \) and \( \mu_{\text{fulvic}_{532}} \) denote the absorption coefficients of pure SRFA at the indicated energies. These absorption coefficients were calculated from absorption maps measured under dry conditions. \( \text{OD}_{532} \) was assumed to remain constant. \( \mu_{\text{H}_2\text{O}} \) is the absorption coefficient of water at 550 eV taken from the literature [Chantler, 1995]. Note that this is only an approximation for the water thickness, as we assume here no absorption from water in \( \text{OD}_{532} \) and the ratio of \( \text{OD}_{\text{fulvic}_{550}} \) and \( \mu_{\text{OD}_{532}} \) to remain constant also in the humidified sample.

**Tannic acid preparation** The tannic acid (Figure 4.1) was purchased from Sigma Aldrich and was not further purified. To generate aerosol particles a solution of 5 g/l of tannic acid was nebulized using a home built ultrasonic aerosol generator. The aerosol particles were dried by passing them through a silica gel diffusion dryer, charged using a corona charger and deposited electrostatically on the silicon nitride window. The particles were simultaneously characterized using a SMPS (Scanning Mobility Particle Sizer); a mean diameter of 400 nm was found.

**SRFA sample preparation** The SRFA was purchased from the International Humic Substance Society (IHSS), product number 1S101F. Using MilliQ water, solutions of SRFA were prepared with a concen-
4.3. Experimental Section

Figure 4.1: chemical structure of tannic-acid

tration of 2.6 g/l as suggested by Myneni et al. [Myneni et al., 1999]. The pH of the solution was 2.56. No salts were added to the solution. Additionally, SRFA was fractionated into different molecular size using ultrafiltration. The ultrafiltration and their characterization is described elsewhere [Dinar et al., 2007]. Two fractions were chosen for the investigations. Fraction F2 having a molecular weight ranging from 0.5-1.0 kDa with pH 2.4 and fraction F5 ranging from 10-30 kDa with pH 2.45. Droplets of the solutions with a volume of about 60-180 pl were generated using a piezoelectric dispenser. The sample holder was placed on a horizontally movable microstage, so that a droplet pattern was generated. The deposited particles were air-dried such that round fulvic acid droplet residues of 30-40 µm remained on the window, see Figure 4.2. This sample will be further referred to as ‘bulk’. A further unfractionated SRFA sample was also generated using the nebulizer method described above. Both methods guaranteed sample free regions to measure $I_0$. The microdispenser method can be applied to small precursor solution volumes (0.5 ml), while the nebulizer methods needs a sample volume of at least 10 ml.

HULIS preparation The HULIS were sampled during the LBO day in 2008 at the Weizmann Institute. During these celebrations a lot of wood is burned. The HULIS were extracted using the protocol described by Dinar et al [Dinar et al., 2007].

4.3.1 The microreactor

A detailed description of the microreactor is found elsewhere [Huthwelker et al., 2010]. It will be only shortly described here. The microreactor, which fits into the standard sample holder of the microscope, is a small chamber with two silicon nitride windows that allow X-ray transmission. The reactor consists
of two parts: the sample holder and the body of the reactor which comprises the gas inlet/outlet and the temperature control. The aerosol particles or droplets are deposited on the window of the sample holder, which is then screwed onto the other part of the microreactor. A dewar filled with liquid nitrogen is connected to the microreactor via a copper wire. A heating mounted on the microreactor was used to adjust the temperature in the reactor to 20 °C. This type of temperature control required that the microscope chamber was evacuated to about $10^{-2}$ mbar. To avoid window breaking, the pressure in the microreactor was set to 150 mbar. A humidified flow of helium (20 ml/min) was passed through the reactor. First results with the microreactor showing the operational reliability were reported elsewhere [Zelenay et al., 2011].

4.4 Results and Discussion

4.4.1 Carbon NEXAFS spectra

Even though C-edge NEXAFS spectra are compound specific, the analysis of complex organic molecules or mixtures is limited to the retrieval of functional groups. At 285 eV the $1s \rightarrow \pi^*$ transition of unsaturated carbon (further denoted as aromatic-C) is observed. At 286.6 and 288.6 eV, the $1s \rightarrow \pi^*$ transitions of O-substituted aromatic carbon such as phenols (phenol-C) and carboxyls (carboxyl-C) are monitored, respectively. Furthermore, the presence of O-alkyl carbon (O alkyl-C) can be observed at 289.5 eV, and the carbonyl transition (carbonyl-C) at 290.5 eV. All spectra were background subtracted and normalized to 310 eV.

Figure 4.3 a) shows the NEXAFS spectrum of the fraction F2 of the SRFA sample. These spectra are well known [Hopkins et al., 2007, Claret et al., 2008, Schumacher et al., 2006]. Aromatic-, phenol- and carboxyl-C transitions are observed at 285, 286.6 and 288.5 eV, respectively. In b) the spectrum of the fraction F5 is shown. Again, the three typical absorption features are observed. The comparison of
4.4. Results and Discussion

these two spectra shows that in the fraction F2 lower aromatic/phenol-C but higher carboxyl-C content is found. Note again, that these spectra were taken from droplet residues, i.e., after drying of the solution droplet on the substrate and before any new exposure to elevated humidity. As discussed later, in the unfractionated SRFA strong variations in functional groups depending on sample location are observed. Such variations are not observed in the fractionated samples. The only morphological variations found in the dry droplet residue were small inclusions of around 500 nm where the phenol-C content was apparently higher.

Spectrum c) depicts the carbon K-edge spectrum of tannic acid. High absorption intensities are found at 285, 287.1, 288.1, 288.9 and 289.5 eV. All these transitions correspond well with the chemical structure of tannic acid. This spectrum could be considered being composed of the spectra reported for gallic acid and rhamnose [Solomon et al., 2009]. Gallic acid shows a high absorption intensity at 285.1 eV, attributed to \(1s \rightarrow \pi^*\) transition of an aromatic-C, at 287.3 eV which was assigned to the \(1s \rightarrow \pi^*\) transition associated with the phenolic O-H group, at 288.3 eV attributed to the \(1s \rightarrow \pi^*\) transition of carboxyl-C and at 289.32 eV assigned to the \(1s \rightarrow \pi^*\) transition of the carbonyl-C. The rhamnose monohydrate shows absorption intensities at 288.47 and 289.44 eV which were attributed to the \(1s \rightarrow 3p/\sigma^*\) transition of O-alkyl moieties [Solomon et al., 2009].

Figure 4.3 d) shows carbon K-edge spectra of the HULIS sample. The spectrum is characterized by a low and broad shoulder between 284.5 and 286.5 eV indicating only low amounts of aromatic- and phenol-C. The spectrum is dominated by the strongly increasing absorption intensity at 288.8 eV indicating the predominance of carboxyl-C and O-alkyl moieties. This was also observed by tandem mass spectrometry measurements [Dron et al., 2010]. The spectrum resembles very much those obtained from wood burning particles or secondary organic particles, which also exhibited similarly low aromatic content and indicated the presence of highly oxidized carbon compounds such as polyacids and polyols [Braun, 2005, Bahadur et al., 2010]. This would be consistent with the view that high amounts of secondary organic and humic like substances are associated with particles from biomass burning events [Dron et al., 2010].

4.4.2 Oxygen NEXAFS spectra

Figure 4.4 shows the oxygen K-edge spectra of the different compounds. All spectra were background subtracted and normalized to 560 eV. At 532 eV the \(1s \rightarrow \pi^*\) (e.g. from carboxyl or ketone) transitions are observed. At around 540 eV a broad absorption intensity stemming from the \(\sigma^*\) transition of e.g. alcohol, ketone or carboxyl is observed. Figure 4.4 a) shows the O K-edge spectrum of the fraction F2 of SRFA. A high absorption intensity can be observed at 532.5 eV as well as a broad shoulder at 539 eV. Compared to the spectrum of fraction F5, depicted in Figure 4.4 b), the absorption at 532.5 eV is
more pronounced, which is consistent with the higher carboxyl-C fraction, and the absorption feature at 539 eV appears broader. Spectrum c) in Figure 4.4 shows the O K-edge spectrum of tannic acid. This spectrum is in good agreement with the NEXAFS O K-edge spectrum of tannic acid measured by Hu et al [Hu et al., 2008]. A high absorption intensity can be observed at 532.3 eV. This transition is again ascribed to the $1s \rightarrow \pi^*$ transition of C=O of e.g. carboxyls. A broad absorption intensity is observed at around 535.5 and 540 eV, which was assigned to the $\sigma^*$ transition of O-H and O-C bonds [Hu et al., 2008].

Spectrum d) shows the absorption spectrum of the HULIS sample. Also here we find an absorption at 532.3 eV and a broad absorption intensity at 538.3 eV. As the absorption intensity at 532.3 eV is not strong, mainly O-alkyl moieties are supposed to be present.

### 4.4.3 Water uptake in tannic acid

The water uptake behavior of tannic acid was investigated using submicron particles generated with the nebulizer. Figure 4.5 shows the absorption maps recorded at 560 eV of one single tannic acid sub-
micron particle at different RH. At this energy no resonant absorption is expected. Thus the increase in absorption intensity at this energy reflects the amount of additional oxygen taken up in response to the changes in humidity, hence the amount of water molecules associated with the particle. Figure 4.5 a) shows the particle at 40 % RH (relative humidity). The increase in total absorption intensity (integrated over the whole particle) is about 13 % when RH was increased to 80 % RH (Figure 4.5b), respectively. This indicates only small amounts of water taken up by the particle. In average this results in a water column of 25 nm. This is also supported by the profiles taken from the particle shown in the lower panel of Figure 4.5, where no strong deviation from the profile at 0 % RH is observed. The particle changed significantly when RH was increased to 90 % RH. The particle grew from about 600 to 800 nm, simultaneously the profile of the particle changes significantly, the symmetrical shape of the profile indicates a hemispherical shape of the particle. An increase in the total absorption intensity by about 70 % is observed, which indicates a large water uptake corresponding to an average water column of about 95 nm. This behavior is confirmed by the calculated O/C ratios. O/C ratios were calculated assuming only oxygen and carbon being present in the sample. Hereby pre- and post-edge absorbance were compared with theoretical values from Chantler et al [Chantler, 1995]. An O/C ratio of 0.53 for the

Figure 4.4: Oxygen K-edge spectra of a) the fraction F2 of SRFA, b) the size fraction F5 of SRFA, c) tannic acid and d) HULIS, all spectra were measured at 0 % RH.
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dry particle is found, which is close to the theoretical value of 0.605. At 80 % and 90 % RH O/C ratios of 0.55 and 1.1 are found, respectively. This would be an approximate water to tannic acid molar ratio of 40 at 90 % RH. This corresponds roughly to one water molecule per oxygen in tannic acid at 90 % RH. Qualitatively, these measurements are consistent with experiments performed by Cowen et al. [Cowen and Al-Abadleh, 2009], who also found continuous water uptake but did not quantify the amount of water.

Figure 4.5: Upper panel shows absorption images of a tannic acid particle which was deposited as aerosol particles obtained at a) 40 % b) 80 % and c) 90 % RH. The images were measured at 560 eV. The lower panel shows a vertical profile through the particle.

Additionally, NEXAFS spectra at the oxygen edge were measured at different RH. Note again, that only one spectrum was recorded per single particle. Figure 4.6 a) shows the tannic acid spectrum measured at 0 % RH, which is the same spectrum as depicted in Figure 4.4 c), see discussion above. When increasing RH to 42 % only a small relative decrease in the absorption intensity at 532.3 eV is observed. This change corresponds to the addition of water in the spectrum since the NEXAFS spectrum of water does not show an absorption intensity at 532 eV [Myneni et al., 2002, Naslund et al., 2005, Wernet et al., 2004]. At 60 %, Figure 4.5 c), the spectrum does not reveal additional changes. In spectrum d), measured at 85 % RH, the absorption intensity at 532 eV decreased significantly and a strong absorption intensity at 539 eV evolves, which corresponds to the absorption of water [Cavalleri et al., 2002, Tzvetkov et al., 2008]. At 95 % RH, see spectrum e), the absorption intensity at 532 eV further relative decreased with the main edge being similar to the spectrum of water depicted in Figure 4.6 f).
4.4. Results and Discussion

Figure 4.6: O K-edge spectra of tannic acid at different RH a) 0 %, b) 42 %, c) 59 %, d) 85 % e) 95 % f) water spectrum normalized at 560 eV. The spectrum of water was adapted from Tzvetkov et al. [Tzvetkov et al., 2008].

4.4.4 Water uptake in SRFA

Aerosol particles

The same water uptake analysis was performed with SRFA submicron particles generated using the nebulizer. Figure 4.7 shows absorption images of a single submicron particle measured at 0 % Figure 4.7 a), 80 % b) and 90 % RH c). The absorption intensity increases by 25 % when RH is set to 80 %, which corresponds to a water column of about 15 nm on average. Simultaneously the particle grows from 400 nm to 500 nm in diameter and continues growing when RH is set to 90 %. Thereby the absorption intensity at the oxygen edge increases by 125 %. This corresponds to an average water uptake of about 100 nm. The O/C ratios increase from 0.28 at 0 % to 0.5 at 80 % and 0.75 at 90 % RH, respectively. This corresponds roughly to one and two water molecules per oxygen in SRFA at 80 and 90 % RH, respec-
tively. Here, a large deviation is found from the elemental composition as provided by the IHSS, which indicate an O/C ratio of 0.6.

The analysis of the morphology shows that the particles always look homogeneous. But this might also stem from the insufficient resolution of the microscope which can not resolve the microstructure of inhomogeneities smaller than 40 nm. It is not possible to exclude one of these scenarios based on our measurements.

**Figure 4.7:** Upper panel shows absorption images recorded at 580 eV of an SRFA deposited aerosol particle measured at a) 0 % rh b) 80 % and c)90 %. The lower panel shows profiles through center of the particle.

In addition to this analysis, oxygen spectra of single submicron particles at different RH were recorded, see Figure 4.8. Figure 4.8 a) shows a spectrum of SRFA measured at 0 % RH. Again, the $\pi^{*}$ and $\sigma^{*}$ transitions of oxygen at 532 and 539 eV are observed, respectively. Similar to the case of tannic acid, the increasing contribution of water to the absorption spectrum with increasing humidity is obvious from the decreasing absorption intensity at 532 eV and the increasing intensity at 539 eV for the spectra shown in Figure 4.6 b) to e).

Dinar et al. measured the hygroscopic growth (GF) of SRFA aerosol using a HTDMA (hygroscopic tandem mobility analyzer). GF's of 1.02 at 50 %, 1.04 at 68 %, 1.06 at 81 % and 1.15 at 90 % RH were found. These findings confirm our observation of continuous water uptake with significant additional water uptake between 85 % and 90 % RH. Quantitative comparison of these GF with our O/C ratios under humid conditions would require knowing the density as a function of humidity. The direct correlation of the increase in diameter with the volume increase is not possible as the absorption coefficients of the fulvic acid at different RH are unknown.

In comparison with tannic acid, in SRFA higher water uptake is observed which is related to the lower aromatic/phenol-C but higher carboxyl-C content of SRFA.
4.4. Results and Discussion

Figure 4.8: O K-edge NEXAFS spectra of fulvic acid measured at a) 0 % b) 50 % c) 70 % d) 80 % RH e) at 90 %

Bulk SRFA

Here, the spatially resolved chemical analysis of the bulk SRFA sample is discussed, first for the dry droplet residue. The region investigated is indicated in Figure 4.2 by a rectangle; an overview over this region is displayed in Figure 4.9, upper panel.

Figure 4.10 shows chemical maps measured at 285 (upper panel), 286.6 (middle panel) and 288.5 eV (lower panel) divided by the chemical map measured at 310 eV to represent the spatially resolved relative contribution of the corresponding functional groups. The region marked in black indicate locations with over-absorption (OD > 1.2).

The images show that the functional groups in the dry SRFA droplet residue are inhomogeneously distributed over the investigated region. Higher phenol- and aromatic-C content is found at the right border of the selected region while carboxyl-rich compounds show an opposite distribution. This trend is
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Figure 4.9: Upper panel: absorption map of investigated region measured at 310 eV to represent the carbon distribution. Lower panel: Compound map showing the distribution of functional groups with region 1 having high amounts of carboxyl, region 2 showing high amount of phenols and aromatic functional groups, but at the carboxyl energy, overabsorption is measured and region 3 showing high amounts of phenol- and aromatic- and low amounts of carboxyl-C.

also confirmed by the spectra which where recorded in the same droplet residue from a similar region, see Figure 4.11. Spectrum I stems from the border of the droplet residue, spectrum II corresponds to the middle part of the section (the part with over-absorption was not included) and spectrum III stems from the carboxyl-rich region (‘left’ part in Figure 4.10). Figure 4.9 (lower panel) shows a ‘compound map’ summarizing the distribution of the chemical functional groups. Region 1 shows high carboxylic content, on the other hand the region 3 shows high phenolic and aromatic content. Region 2 was not entirely characterized, since over-absorption influenced the analysis.

O/C ratios, calculated from carbon maps, of 3.3 (region 1), 2 (region 2) and 1 (region 3) were found. All ratios clearly overestimate the oxygen content, which might be caused by the weak absorption of the elements at the carbon pre-edge. This calculation becomes even more problematic when O/C ratios from NEXAFS spectra are calculated as less measurements points are available. However, the oxygen absorption maps give more reliable values due to the higher cross section of carbon. The O/C ratios range from 0.75 (region 3) to 0.6 (region 1 and 2).

The ratios of the aromatic,- phenol- and carboxyl-C intensity in region 1 correspond very well to the corresponding ratios in the fraction F2. These ratios found in region 3 agree well with the ones found in fraction F5.

Figure 4.10: colorbar, upper panel: relations of 285/310 eV, the colorbar, i.e. OD values, ranges from 0.1-0.6, middle panel 286/310 eV the colorbar ranging from 0.2-0.8, lower panel 288/310 eV with OD ranging from 0.7-1.8
4.4. Results and Discussion

Figure 4.11: C K-edge NEXAFS spectra taken from the dry droplet residue, I measured at the border of the particle, III in the middle of the droplet residue, II in the region in between with highest C content, whereby locations with OD > 1.2 were omitted. These regions I, II, and III roughly correspond to 1, 2 and 3 in Figure 4.10, respectively.

These images and spectra show that SRFA experienced a first separation upon drying on the silicon nitride window. While the droplet dried, i.e. the water evaporated, aromatic compounds precipitated and remained at the border of the droplet. Interesting are the small inhomogeneities as indicated by an arrow in Figure 4.10. These inclusions show lower carboxylic-C compounds than their surrounding and have a typical size of around 400 nm. It is unknown if these inclusions were generated during the drying process or if they remained undissolved in the solution, which was used unfiltered for sample generation. In the droplet residue of fractionated SRFA samples (F2 and F5) comparable inclusions were found, but to a lower extent.

**Humidified bulk sample**

Exposing the sample to 95 % RH led to significant uptake of water and a drastic reorganization of the different compounds within the region. This is clearly demonstrated by the absorption maps in Figures 4.12 and 4.13 in terms of the spatial distribution of carbon and oxygen, respectively. At larger scales, it appeared that in this case a solution formed from material in the middle and tended to move towards the border, where it (partially) mixed with the material there. It is also directly apparent from the comparison of images in Figures 4.12 and 4.13 that different aqueous solutions or likely also other forms of hydrated organic phase must have formed. Similar inhomogeneities as discussed below were also observed in other regions, data not shown.

Interesting is the relative distribution of the functional groups. Figure 4.14 shows chemical maps mea-
Figure 4.12: Upper panel: transmission image measured at 310 eV, the OD values range here from 0 (violet) to 1 (yellow). Middle panel: ratio 278 / 310 eV, showing OD ratios between 0.25 and 0.8. Lower panel: Map of the distribution of functional groups, the regions are explained in the text.

Figure 4.13: Upper panel shows the absorption map measured at 550 eV, the OD ranges from 0 to 0.4. Middle panel shows the ratio 532 / 550 eV, the ratios vary from 0.15 to 0.5. Lower panel shows the corresponding absolute water column from 0 (yellow) to 600 nm (dark blue).

These images show that the different functional groups of SRFA are inhomogeneously distributed over the investigated region. The spatially resolved chemical characterization is discussed in conjunction with Figure 4.14 and the water uptake ability within the different regions in conjunction with Figure 4.13. The middle panel of Figure 4.12 shows the ratio of the absorption maps measured at 278 eV divided by the absorption map measured at 310 eV. Since oxygen absorbs about two times more at the pre-edge of carbon (i.e. 278 eV) and carbon about 15 times stronger at 310 eV, strong relative accu-
Figure 4.14: Chemical maps of aromatic (upper)-, phenol (middle)- and carboxyl (lower panel)-C divided by chemical map measured at 310 eV are depicted. The ratios vary from 0.2-1.3 in the upper, 0.2-1.5 in the middle and 1-3 in the lower panel, the black bar indicates a size of 3 µm.

mulation of carbon and oxygen can be observed independently of their absolute thickness. Thus, in violet (Figure 4.12, middle panel), are marked regions with high carbon content while the yellow regions show strong accumulation of oxygen, i.e. high water amount associated within the region. The same information is revealed when absorption maps of images measured at 310 eV and 550 eV are compared, see Appendix.

The same region was also measured at the oxygen edge. Figure 4.13 (upper panel) shows the absorption map of this region measured at 550 eV. The middle panel shows the ratio of the chemical maps measured at 532 and 550 eV. At 532 eV the water spectrum does not show any absorption intensity [Myneni et al., 2002, Naslund et al., 2005, Wernet et al., 2004], see also Figure 4.8. At this energy only the π* transition of C=O is found. In the chemical map at 550 eV no resonant absorption is measured. Therefore, this ratio indicates the relative occurrence of organic compounds. It shows a similar distribution as shown in Figure 4.12. Besides large structures as discussed for this region of several µm, also smaller likely colloidal type particles were observed of only few hundred nm in the lower part of the image.

Our investigations are consistent with measurements of Diallo et al. [Diallo et al., 2005] who observed fractal aggregates with primary particles of a radius of gyration > 242 nm in SRFA solutions.

Figure 4.13 (lower panel) shows the absolute water column of the discussed section calculated using equation 4.1. It reveals that also the absolute water column shows a complimentary structure to the distribution of the organic compounds. Hereby we find that in the low water uptake region about one water molecule and in the high water uptake region about four water molecules are associated per oxygen of SRFA, respectively. The region with low water uptake is therefore comparable to tannic acid considering the water uptake only.
This separation of high and low water uptake region can be characterized by the occurrence of high and low relative amounts of carboxyl- and aromatic-C, and low and high content of phenol-C, respectively, as analyzed by PCA-CA, see Appendix.

This rough analysis can be further refined using ratios of chemical maps (see Appendix) measured at distinct energies, which reveals further small variations in the composition. To discuss these structures the region was divided into 13 different areas (Figure 4.12), whereby region 2 is optically very thin so that the signal to noise ratio is very low. Thus this region will be skipped. The carboxyl-poor region was subdivided into five different areas (region 3, 4, 5, 6, and 10) which showed different chemical profiles. E.g. region 3 shows very high aromatic content as well as large amount of phenol-C and rather low amounts of carbonyl- and O-alkyl-C and comparably low amount of carboxyl-C. Region 4 shows high content of phenol-, aromatic-, O-alkyl-, carbonyl-C. The region marked with 5 shows a more pronounced O-alkyl-C occurrence compared to region 4. Region 6 shows high content of phenol-C and comparably low carboxyl-C content. In region 10, the analysis showed a large amount of aromatic-C, but also O-alkyl and carboxyl-C were abundant. The analysis the ratios of 532 and 560 eV revealed lowest water content associated within the compound mixtures in regions 3, 4 and 6.

The carboxyl-C rich region was divided up into six areas (1, 7, 8, 11, 12 and 13). Highest water uptake show region 11, 12 and 13. Regions 12 and 11 are very similar in the composition (high carboxyl-, O-alkyl-, carbonyl-C and low phenol-C), but region 11 shows a higher aromatic-C content. Region 13 shows high aromatic-C and low phenolic-, O-alkyl-, carbonyl-C content. Regions 7 and 8 show moderate water uptake and are as well similar in their composition showing high phenol-, aromatic- and carboxyl-C content whereas in region 7 a higher phenol-C and lower aromatic-C content was observed. Region 1 shows less water uptake compared to region 7 and 8. The composition shows high amount of carboxyl- and aromatic-C, and low phenol-C.

The comparison of these different regions reveals that the water-rich regions are best comparable with the fraction F2 due to their high carboxyl-C content and the water-poor regions show best agreement with fraction F5 as they show a high content in phenol-C. This is in agreement with the water uptake behavior of the fractionated SRFA observed in HTDMA measurements where larger growth factors were found for small molecular weight fractions [Dinar et al., 2007].

The tannic acid is not comparable to any of these regions, but its phenol to carboxyl-C ratio fits best with region 6 and its aromatic- to phenol-C ratio is also comparable with the water-rich regions due to its relative low phenol-C content. Similar ratios are found in HULIS. Region 6 shows comparable aromatic- to phenol-C ratios, while region 8 show similar phenol- to carboxyl-C ratios, which makes the SRFA sample at least partly to a representative sample mixture of this HULIS sample.

This experiment shows that in SRFA the water uptake can be related to the relative occurrence of different functional groups. The approximate chemical breakdown can be refined with the relative oc-
currence of phenol-, aromatic-, O-alkyl- and carbonyl-C groups where phenol-C lowers water uptake while the addition of carbonyl-, O-alkyl- and carboxyl-C can increase water uptake ability in the compound mixtures.

4.5 Conclusions

The water uptake in single submicron particles consisting of tannic acid and SRFA was investigated. Tannic acid as well as SRFA showed both continuous water uptake with largest uptake above 85 % RH. This is consistent with the observation by Dinar et al. [Dinar et al., 2007] and Cowen et al. [Cowen and Al-Abadleh, 2009]. At 90 % RH we found one water molecule associated with one oxygen of tannic acid, while in SRFA two water molecules were found per oxygen in SRFA. The bulk SRFA sample as obtained after drying of a droplet on the silicon nitride window showed spatially separated regions with different chemical composition. Phenol- and aromatic-rich compounds precipitated earlier during the drying process and remained at the border of the droplet residue. When increasing RH to 95 % in situ, considerable reorganization of the material occurred with phase separation along the carbon functional group composition showing up at different spatial scales. The PCA-CA analysis of the compound mixture reveals that a gross differentiation can be made into two classes of material, one with carboxyl/aromatic-C rich and phenol-C poor composition showing high water uptake at 95 % RH and one with opposite relative composition showing low water uptake. The water uptake behavior of the phenol-C rich region was shown to be comparable to the water uptake behavior of tannic acid. Within these two classes of regions, additional variability in water uptake could be related to variations in other carbon functional groups. E.g. an increased content in O-alkyl groups was shown to increase water uptake, while high O-substituted aromatic compounds impeded water uptake. The morphology of the water-rich/poor regions varied strongly. The gross structures of the water-poor region exceeded 10 µm but also structures in the range of 400-500 nm were observed. Since the difference in carbon functional group composition within the two gross classes was similar as that between the fractions F2 and F5, which are rich in carboxyl-C and O-substituted aromatics, respectively, the possible conclusions is that the water uptake ability and the associated spatial separation is also a driven by molecular size. Comparison with an authentic HULIS sample indicate similarities with only few of the separated subregions within the SRFA sample.
4.6 Acknowledgements

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4.7 Appendix

Figure 4.15 shows ratios of absorption maps measured at 310 eV divided by the absorption map measured at 550 eV. Yellow colored regions show the carbon-rich region while in violet are shown the oxygen-rich regions.

![Figure 4.15](image_url)

**Figure 4.15**: Ratios of the absorption map measured at 310 eV divided by the absorption map at 550 eV. The color bar range from 1.1 (violet) to 2.9 (yellow).

Figure 4.16 shows the PCA-CA analysis of the wet bulk SRFA using axis2000 [Hitchcock, 2006]. Two main regions can be identified, a carboxylic/aromatic-C rich region colored in yellow, and a phenol-C rich region colored in red. Note that the PCA-CA analysis did not reveal any further structural features. The interpretation of region with overabsorption at 288.5 eV, see Figure 4.14 needs to be done carefully.

Figure 4.17 shows ratios of chemical maps measured at different energies. Upper panel shows ratios of aromatic-C and phenol-C, middle panel shows ratios of aromatic-C and carboxyl-C, and lower panel shows the ratios of phenol-C and carboxyl-C.
4.7. Appendix

Figure 4.16: PCA-Cluster analysis, which revealed two regions.

Figure 4.17: upper panel: ratios of chemical maps measured at 285 and 286 eV, OD varies from 0.4 to 1.2; middle panel: ratios from chemical maps measured at 285 and 288 eV OD varies from 0.2 to 0.5; lower panel shows ratios of 286 to 288 eV whereby OD varies from 0.1 to 0.7.

4.7.1 Experiments on beam damage

Because organic material is sensitive to beam damage [Schäfer et al., 2009], several beam damage experiments were performed with SRFA. Mass loss and degradation of single function groups was investigated upon exposure to the x-ray beam. Figure 4.18 illustrates the results of the beam damage experiment upon exposure of SRFA to the beam measured at 320 eV. The OD of the sample decreased by 15 % upon exposure for more than 300 ms. The error bars show the corresponding standard deviations.
Single chemical functional groups show different sensitivity to radiation damage. Thus seven stacks with large energetic resolution were measured (0.5 eV steps until 292 eV and 1 eV steps until 320 eV) on one single SRFA deposited aerosol particle. These spectra were modeled using Gauss fits and an arctan function to model the ionization point [Outka and Stohr, 1988]. The maxima of the Gauss fits were fixed at the main absorption intensities of SRFA, 285, 286.6, and 288.5 eV and at 287.4, 289.5, 290.2 and 292.2 eV. From this chemical breakdown, the single contributions were plotted. Except for the carboxyl-C at 288.5 eV the fits showed no trends and remained the same within error. Figure 4.19 shows the contribution of the carboxyl-C versus the exposure time to the x-ray beam. In this case a decrease in the absorption intensity is observed to around 83 % of its original value after 350 ms exposure time. Usually, an exposure of around 150 ms is used to record a whole image stack. In this case the decrease in absorption intensity is only around 10 %, the loss in absorption intensity of the carboxylic group is even less than 10 %.

**Figure 4.18:** beam damage experiment with standard deviation, measured at 320 eV under dry conditions

**Figure 4.19:** Gauss fits from the electron transition at 288.5 eV measured under dry conditions.
Bibliography


Chapter 5

Aging fingerprints in combustion particles

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5.1 Abstract

Soot particles can significantly influence the Earth's climate by absorbing and scattering solar radiation as well as by acting as cloud condensation nuclei. However, despite their environmental (as well as economic and political) importance, the way these properties are affected by atmospheric processing is still a subject of discussion. In this work, soot particles emitted from two different cars, a EURO 2 transporter, a EURO 3 passenger vehicle, and a wood stove were investigated on a single-particle basis. The emitted exhaust, including the particulate and the gas phase, was processed in a smog chamber with artificial solar radiation. Single particle specimens of both unprocessed and aged soot were characterized using x-ray absorption spectroscopy and scanning electron microscopy. Comparison of the spectra from the unprocessed and aged soot particles revealed changes in the carbon functional group content, such as that of carboxylic carbon, which can be ascribed to both the condensation of secondary organic compounds on the soot particles and oxidation of primary soot particles upon photochemical aging. Changes in the morphology and size of the single soot particles were also observed upon aging. Furthermore, we show that the soot particles take up water in humid environments and that their water uptake capacity increases with photochemical aging.

5.2 Introduction

The Earth's radiation balance is strongly affected by atmospheric aerosol particles, which absorb and scatter radiation (direct effect) or act as cloud condensation nuclei (indirect effect). In contrast to most aerosols, which cool the atmosphere by scattering radiation, soot particles, containing black carbon, warm the atmosphere by absorbing sunlight. This contribution is estimated to be the second only to carbon dioxide [Jacobson, 2001] and depends heavily on the source of the soot particles and their atmospheric processing (i.e., their mixing state with transparent and hygroscopic aerosol components). Such processing can change the light scattering and absorption properties (such as the single scattering albedo) of the soot particles [Adachi et al., 2010] as well as their lifetime in the atmosphere. During atmospheric processing, the physical and chemical properties of soot particles are continuously altered through condensation and evaporation of various organic and inorganic compounds [Saathoff et al., 2003], coagulation with, e.g., sulfate particles [Worringen et al., 2008], oxidation [Peters et al., 2006], and restructuring [Abel et al., 2003]. Such processing introduces large uncertainties in the quantitative evaluation of the radiative forcing of atmospheric soot particles [Moffet and Prather, 2009]. Therefore, because the properties of atmospheric soot particles are highly variable and also strongly impact the Earth's radiation balance, experiments that further our understanding of these particles are essential to our understanding of, and ability to accurately model, the Earth's climate.
Coating experiments have previously been performed under defined laboratory conditions using, for example, carboxylic acids [Xue et al., 2009] or sulfuric acid [Zhang et al., 2008], in which changes in morphology were observed. [Xue et al., 2009] reported that coating soot particles with glutaric and succinic acid increased both light scattering (up to 3.8 fold) and light absorption (less than 1.2 fold). While such laboratory experiments are useful in providing detailed information on the physical properties of processed particles, they do not represent the breadth of atmospheric processing that environmentally relevant soot particles are subject to, which is certainly much more complex [Robinson et al., 2007, Hamilton et al., 2004, Saathoff et al., 2003, Weingartner et al., 1997].

Atmospheric aging of soot has been assessed via aircraft [Schwarz et al., 2008] and balloon measurements [Renard et al., 2005] and indicate a fast mixing of soot particles with, for example, sulfate species [Johnson et al., 2005] and coating with secondary organic products [Moffet and Prather, 2009]. This fast mixing impedes a direct comparison of fresh particles with their corresponding aged particles.

Filling the gap between laboratory and field studies, smog chamber experiments are ideally suited to following the evolution of secondary organic aerosols (SOAs) generated from the photo-oxidation of volatile organic compounds (VOC’s). Some examples of such experiments that are related to the present investigation, were performed with exhaust from a diesel power generator [Sage et al., 2008, Weitkamp et al., 2007] as well as from biomass burning [Grieshop et al., 2009]. This photochemical processing of exhaust is assumed to be the dominant soot aging mechanism, which is also directly related to the radiative properties of soot [Moffet and Prather, 2009]. Therefore, smog chamber experiments provide the possibility to observe atmospheric like processing under controlled conditions [Paulsen et al., 2005].

This paper reports, for the first time, a combined investigation of morphological and chemical modifications, including hygroscopic properties at the single soot particle level for atmospheric like processing in a smog chamber.

### 5.3 Experimental Section

#### 5.3.1 Sample preparation

All soot samples were sampled from the smog chamber [Paulsen et al., 2005] located at the Paul Scherrer Institut (PSI), Switzerland. A detailed description of the experiments is given by [Chirico et al., 2010] and [Heringa et al., ] and will be only briefly described here. The smog chamber, a Teflon bag with a volume of 27 m$^3$, is temperature controlled within the range of 20-25 °C. Sunlight irradiation is simulated with four xenon arc lamps with a cutoff at 280 nm. Different online particle analysis instruments were operated during the experiments, such as a scanning mobility particle sizer (SMPS), a volatility and
hygroscopic tandem differential mobility analyzer (V/H-TDMA) [Duplissy et al., 2009, Tritscher et al., 2011], and an Aerodyne, high resolution, time-of-flight, aerosol mass spectrometer (AMS) [DeCarlo et al., 2006], to provide complementary data to compare with the single-particle measurements. Note here that the AMS measures only compounds which evaporate at 600 °C and hence, the refractory part of soot is not included in the AMS measurements.

Emissions were sampled from two different cars, a EURO 2 Volkswagen Transporter TDI Syncro from December 2000 (not equipped with a catalytic converter), a EURO 3 Opel Astra 2.0 DTA from February 2002 (equipped with a diesel oxidation catalyst (DOC)), and a log wood stove (Attika Avant). The unfiltered exhaust gas of the two cars was diluted with particle-free, preheated (150 °C) air by a factor of seven immediately after emission. The exhaust was led through a heated (150 °C) injection system into the indoor smog chamber with a final dilution ratio of around 1:120 [Chirico et al., 2010]. The transfer and dilution system for the exhaust from the wood stove was heated to 80 °C. One hour after injection, the arc lamps in the smog chamber were turned on to begin irradiation. In case of the car exhaust samples, ozone was introduced into the smog chamber to oxidize NO to NO$_2$, prior to irradiation. Once the lamps were switched on, propene (which is not a SOA precursor [Cocker et al., 2001]) was added to increase the VOC/NO$_x$ ratio and to raise the OH levels. Both cars were started with cold motors and were run idle during injection.

Note that the STXM-NEXAFS measurements of the aged and fresh diesel combustion particles stem from processes conducted on different days but with identical processing and sampling conditions. For example, AMS measurements show a comparable increase in organic compounds. Also note that the high resolution AMS data from the EURO 3 car, i.e., O/C ratios, were taken from a separate, but identical, experiment run due to a software error during the experiments from which the STXM-NEXAFS samples were prepared.

In the wood stove experiments, the exhaust was injected into the chamber during the flaming phase and the arc lamps were switched on without the addition of ozone or propene.

Particles were sampled before and after aging of the diesel and wood combustion particles in the smog chamber. The unprocessed soot particles were sampled immediately after injection of the exhaust into the smog chamber. After 2 hours of light induced aging, the first changes in hygroscopic properties of the soot particles were observed in the HTDMA and the sampling of the aged soot particles was started. For sampling, the soot particles were pumped out of the smog chamber, with a gas-flow of about 1.2 l/min, charged via a corona charger and deposited electrostatically (0.8 kV) onto a silicon nitride membrane (Silson Ltd., Northampton, UK). The membrane was glued (crystal bond, SPI suppliers, West Chester, USA) onto a small sample holder of the microreactor (see below). For the aged particles, the sampling was run for around four hours between two and six hours after the arc lamps were turned on in order to obtain a reasonable coverage of the membrane substrate. The particle concentration in the
smog chamber was measured to range between 10000-20000 particles cm$^{-3}$.

### 5.3.2 Microreactor

Exposure of the sample to various relative humidity and temperature environments during x-ray measurements in the PolLux microscope was enabled by a custom microreactor (see [Huthwelker et al., 2010] for a detailed description). Briefly, the microreactor consists of two parts: the sample substrate membrane, where the submicron particles are deposited and the body of the microreactor, which includes a capping membrane and a gas flow inlet and outlet. Fixing the two halves of the microreactor results in enclosing the sample particles between two 50 nm thick silicon nitride membranes (with about 300 µm separation). The membranes allow transmission of x-rays for STXM and NEXAFS measurements, while the microreactor gas inlet and outlet allows access to the enclosed volume for control of the sample environment.

The temperature of the microreactor is controlled by the combination of a heater and cooling via a copper braid attached to a liquid nitrogen dewar. The temperature during the x-ray measurements was set to 20 °C. A flow of 20-50 ml/min of helium (at 150 mbar) was passed through the reactor during all measurements. The microscope chamber was evacuated to 10$^{-2}$ mbar in order to reduce attenuation of the x-ray beam. A variable portion of the gas flow through the reactor can be, if required, humidified by passing the gas over a temperature controlled water bath. The relative humidity (RH) is measured using capacitative sensors, operated at room temperature, at the exit line of the microscope chamber. A thermocouple mounted at the microreactor itself is used to enable corrections of the RH for the precise temperature in the microreactor. The RH can be adjusted from 0 to 95 % RH.

### 5.3.3 STXM-NEXAFS analysis

The STXM and NEXAFS analyses were performed at the PolLux beamline [Raabe et al., 2008] of the Swiss Light Source (SLS) located at the Paul Scherrer Institut. Photons in the range of 200-1200 eV are provided by this beamline with an energy resolution ($E/\Delta E$) of about 3000. The end station is equipped with a STXM operated with a spatial resolution of about 40 nm for the present experiments. The calibration of the spectra was performed by measuring the well-defined transitions of polystyrene spheres at the carbon edge [Dhez et al., 2003]. All soot samples were measured in the microreactor [Zelenay et al., 2011a, Huthwelker et al., 2010].

To normalize the spectra and images, the Lambert–Beer law (OD=$-\ln(I/I_0)=d\mu$) was used, with OD being the optical density, $\mu$ the mass absorption coefficient, $d$ the thickness of the sample, $I$ the transmitted light intensity through the particle, and $I_0$ the incident light intensity (measured as the transmitted
light intensity in a particle-free region nearby an individual particle.

All spectra were measured in the image stack mode, i.e., a series of images at closely spaced energy steps [Jacobsen et al., 2000]. These image stacks were taken in energy steps of 0.15 eV in the range of 284-292.5 eV and in 0.3 eV steps in the range of 280-284 and 292.5-320 eV, respectively at the carbon K-edge (C K-edge). At the oxygen K-edge (O K-edge), step sizes of 0.2 eV were used for 532-550 eV and 0.5 eV for 525-532 and 550-560 eV, respectively. Absorption maps were converted from transmission images by applying the Lambert–Beer law. The chemical maps were generated from the absorption maps by subtracting the pre-edge absorption. The spectra were extracted using aXis2000 [Hitchcock, 2006].

5.3.4 Scanning electron microscope

The morphology of the particles was also analyzed using SEM (scanning electron microscope) (Zeiss Supra VP55) with a resolution of 1 nm operated at a voltage of 5 kV. The analysis was performed with the soot particles collected on the same sample holder, i.e., the same day and time, as for the microspectroscopy analysis. Size distributions were extracted from SEM images using the equivalent projected area diameter [Merkus, 2009]. This distribution was obtained by calculating the projected surface area of the particles using threshold images. Qualitative observations and trends of particle sizes are discussed rather than quantitative values, although it was shown that for small agglomerates (<100 nm) this method gives reliable values [Ku and Maynard, 2005]. Note that the sampling of the soot particles took about four hours so that no evolution of the particles sizes can be observed as with the SMPS and therefore averaged SMPS size distributions are shown.

Fractal dimensions were determined from the SEM images [Ku and Maynard, 2005] using the box counting method of ImageJ, a public domain image analysis program developed at the National Institutes of Health.

5.3.5 HTDMA

In this study, data from the H-part (hygroscopicity) of the V/HTDMA (Volatility and Hygroscopicity Tandem Differential Mobility Analyzer) are presented. Dry, monodispersed aerosols are selected in the first DMA. After exposure to high relative humidity (RH) the aerosol particles are scanned with a second DMA coupled to a CPC (Condensation Particle Counter). All instrument parts are accommodated in a temperature controlled housing. The hygroscopic growth factor (GF) is defined as the wet particle diameter (here RH = 95 %) normalized with the dry particle diameter (RH<10 %).

The V/H-TDMA is equipped with a pre-humidification system in front of the first DMA. Particles are ex-
posed to very high RH close to 100 % before they are dried and size selected. Turning the pre-humidifier
on allows restructuring of the fractal soot. The occurrence of restructuring can be identified when pe-
riods with and without pre-humidifier show a different GF.

5.4 Results and Discussion

5.4.1 Particle morphology and size distribution

Size distributions of wood combustion particles are shown in Figure 5.1. The blue bars represent the
size distribution extracted from SEM images of fresh particles. For comparison, the SMPS size distri-
bution is added to the plot as a black line. All size distributions are normalized by the total number of
particles. The size distribution of the projected area diameter for aged particles is shown with red bars.
Again, the SMPS size distribution plot is added, colored grey. The SMPS data show that the mean elec-
trical mobility diameter of the fresh particles is 190 nm. The evaluation of the size distribution using
SEM images shows that most particles have a size between 60 and 250 nm with a tail reaching up to
about 700 nm. The aged particles show slightly larger diameters and also a tail reaching towards larger
diameter (1 µm). This is in agreement with the SMPS data, that shows a shift in diameter to around
240 nm. Obviously, the amount of small particles is somewhat overestimated. This may be related to
the way the soot particles were sampled. Also note that two different kinds of calculations were used
to obtain the size data. We used 2D microscopic images to obtain a diameter, while the SMPS mea-
sures the electrical mobility diameter, see also [Ku and Maynard, 2005]. Figure 5.1 also illustrates SEM
images of single wood combustion particles. The left SEM image illustrates two fresh wood combus-
tion particles, the right one an aged particle. A typical wood combustion particle consists of primary
spherical particles in the range of 40 to 50 nm, which agglomerate to large structures [Vernooij et al.,
2009, Kocbach et al., 2005]. Because the exhaust of the wood burning was sampled during the flaming
phase, no tar balls were found [Vernooij et al., 2009].
The aged wood combustion particles show very often a partly collapsed chain-like structure, especially
in large particles (>800 nm) as shown in Figure 5.1, but the calculated fractal dimensions remains un-
changed within error. 1.81 (± 0.08) was measured for fresh particles and 1.84 (± 0.06) for aged particles.

Figure 5.2 illustrates the different particle size distributions from the EURO 2 car exhaust. The color
code is the same as described for Figure 5.1. The evaluation of the SEM images from fresh particles
shows that most particle sizes are found between 40 nm and 200 nm, also here a small tailing to around
250 nm is observed. The aged particles show a size distribution up to 600 nm. The SMPS measure-
ments show an increase in the mean electrical mobility diameter from 85 nm for fresh particles to 125
Chapter 5. Aging fingerprints in combustion particles

Figure 5.1: Size distributions extracted from the SEM images using the equivalent projected area diameter (bars) and the electrical mobility diameter measured with the SMPS (lines) of the fresh (blue and black) and aged (red and grey) wood stove combustion particles, respectively. The insets are SEM images of a fresh (left) and aged (right) soot particle having projected area sizes of: 205 nm for the small particle and 480 nm for the large particle on the left, and 1 µm for the aged wood particle on the right.

nm upon aging in the smog chamber. Again, SEM images of single particles are depicted in the Figure. Consistent with other authors [Adachi et al., 2007, van Poppel et al., 2005, Kis et al., 2006], primary particles are found with a size of about 30-40 nm aggregated in chains. Inspections by eye do not reveal changes in aggregation of the particles supported by the evaluation of the fractal dimensions which reveals 1.84 (±0.03) for fresh and 1.85 (±0.05) for processed particles, respectively.

Figure 5.2: Size distribution of the particles emitted from the EURO 2 transporter, the red and blue bars represent size distributions from fresh and aged soot particles, respectively. The black and grey lines represent the SMPS size distribution from fresh and aged particles, respectively. The diameters of the particles in the SEM images are: 250 nm for the fresh particle (left) and 300 nm for the aged particle (right).
Figure 5.3 shows the particle size distributions of the EURO 3 passenger car exhaust. The symbols and colors are explained in conjunction with Figure 5.1. While the fresh particles have sizes between 50 and 200 nm, comparable to the particles emitted from the EURO 2 transporter, the aged particles show sizes around 100 nm with a second mode at around 400 nm. In the SMPS such a second mode is not apparent likely because the SMPS only measures until an electrical mobility diameter of 680 nm. However, the SMPS reveals a mean electrical mobility diameter of 80 nm for fresh and 145 nm for aged particles, respectively. The large particle sizes of the processed soot particles might also stem from coagulation on the substrate being enhanced due to electrostatic effects during sampling. SEM images are added in the histogram of a single particle each. Again, the primary particles of fresh and aged soot show the typical size of about 30-40 nm as observed for the transporter. Also in this case, no changes of the aggregation of the soot chains upon soot aging were observed, which is supported by the fractal dimensions being 1.87 ($\pm$0.03) for fresh soot particles and 1.87 ($\pm$0.03) for aged particles. Small changes in the fractal dimensions in the wood stove combustion particles indicate collapsing of the soot chains. The morphology of soot particles stemming from the cars do not seem to be influenced significantly by aging.

The equivalent projected area diameter shows, in general, a comparable particle size distribution as measured by the SMPS and the size increases were also reproduced. These results confirm that the 150-200 nm diameter particles that were chosen for STXM analysis were representative of the total particle populations.

**Figure 5.3:** Size distributions measured using SEM images and the SMPS shown in bars and lines. Blue and red bars, black and grey lines illustrate the fresh and aged particles. The projected area diameter of the illustrated soot particles are 220 nm for the fresh particle (left) and 390 nm for the aged soot particle (right).
5.4.2 STXM-NEXAFS characterization

Figure 5.4 illustrates STXM absorption maps of soot particles from the wood stove (left panel), from the EURO 2 transporter (middle panel) and from the EURO 3 passenger car (right panel).

Figure 5.4: STXM absorption images, measured at 320 eV, of aged soot particles emitted from a) the Attika wood stove with an equivalent projected area diameter of around 500 nm, b) the EURO 2 transporter having a diameter of 260 nm and c) the EURO 3 passenger car with a diameter of about 170 nm. The OD values scale up to 0.5.

NEXAFS spectra from the single particles are shown in Figure 5.5. Each spectrum is taken from the average of a spatial area within a single particle, using the image-stacks described above. Specific chemical species were quantified from the spectra by fitting with Gaussian functions representing characteristic near-edge resonances [Outka and Stohr, 1988], using resonance positions adopted from [Hopkins et al., 2007]. The peak energies were fixed at the C 1s → π* transition of aromatic carbon in benzoquinone (quinone-C, 284.2 eV), the unsaturated carbon (aromatic-C, 285.2 eV), the phenolic or ketone carbon (phenol-C, 286.7 eV), the carboxylic carbon (carboxyl-C, 288.3 eV), carbonyl group (carbonyl-C, 290.5 eV) and the C 1s → σ* transitions of aliphatic carbon (aliphatic-C, 287.4 eV), which overlaps with the C 1s → π* transition of aromatic carbonyl groups, O-alkylic carbon (289.5 eV), the aliphatic/aromatic-C peak (292 eV). An example of such a fit is illustrated in Figure 5.6 and shows the NEXAFS spectrum of an aged wood combustion particle. A broad absorption feature at 305 eV indicates a high π-bond conjugation [Diaz and Hussain, 2007]. Due to the inhomogeneous composition of soot small shifts in the maxima of the transition energies of the single particles are expected. But only the maxima of the peak intensities at 285.3, 288.3 and 292 eV could be unambiguously distinguished for the fit of the spectrum. The maximum of the unsaturated carbon peak shifted from 285.1 to 285.3 eV, while the transition of the carboxyl carbon was assigned between 288.3-288.4 eV. The aliphatic/aromatic-C peak shifted from 292 to 292.2 eV. Note that these energy shifts are close to the energy resolution of the beamline. All other maxima were fixed at the aforementioned values. The peak fitting results are presented in Figure 5.7. Another uncertainty is introduced by the arctangent function representing the ionization edge, whereby the height and slope of this function are unknown for the single particles. Since it can be assumed that more than only one ionization energy is found for the broad variety of carbon species [Outka and Stohr, 1988], the uncertainty is difficult to estimate. The
5.4. Results and Discussion

Spectra were normalized via the area of the whole spectrum.

![Figure 5.5: averaged C K-edge NEXAFS spectra of a) fresh soot emitted from the Attika wood stove (12), b) the corresponding aged soot (19), c) unprocessed soot particles from the EURO 2 transporter (7), d) aged soot particles from the transporter (12), e) unprocessed soot stemming from the EURO 3 passenger car (5), f) aged soot from the passenger car (9), values in brackets define the number of spectra used for averaging.](image)

Spectrum a) in Figure 5.5 shows the averaged NEXAFS spectrum of the fresh wood combustion particle. A distinct absorption at 285 eV and at 292 eV suggests a high aromatic content in the combustion particles. Further, an absorption in the carboxyl-C region (288.5 eV) can be observed, which suggests also a high content in carboxyl-C. The Gaussian fit analysis shown in Figure 5.7 demonstrates that the absorption from quinone-C (284.2 eV) is absent. Furthermore, the analysis shows that fresh wood combustion particles exhibit small absorption at the phenolic-C energy but high transition intensity
from carbonyl-C. However, also alkyl- and O-alkyl-C are involved in the absorption spectrum.

**Figure 5.6:** Example of a gauss fitting of a NEXAFS spectrum for wood combustion particles, the black solid line represents the original spectrum, the red one represents the fit. The maxima of the Gaussian peaks were placed at 284.2 eV (quinone-C), 285.2 eV (aromatic-C), 286.7 eV (phenol-C), 287.4 eV (aliphatic-C), 288.3 eV (carboxyl-C), 289.5 eV (O-alkyl-C), 290.5 eV (carbonyl-C) and at 292 eV (aliphatic-C).

Spectrum b) in Figure 5.5 shows the averaged spectrum of the corresponding aged particles. Again, high absorption intensities are found at 285 and 292 eV, and in the carboxyl-C region. These observations are confirmed by the Gaussian fitting results. While phenol and O-alkyl content slightly increased upon processing, a decrease in carbonyl- and aliphatic-C can be observed. The absorption intensity at 292 eV shows a slight increase. The ratio of the peak heights of the averaged spectra (Figure 5.5) at 285 divided by the peak height at 292 eV is used to quantify the degree of graphitization in carbonaceous materials [di Stasio and Braun, 2006]. This ratio slightly decreases in this case from 0.84 to 0.80 upon aging indicating an increase in alkyl-C and decrease in aromatic-C, which includes also unsaturated carbon. AMS measurements performed by [Heringa et al., ] showed a slight increase at m/z 44, which is attributed to carboxylic groups (\( \text{CO}_2^+ \)), from 10.1 to 10.3 % which correspond well to our carboxyl measurements. The AMS data also shows that photo-oxidation increases the organic carbon by a factor of 3 compared to primary particles. As this increase is significant but yet the NEXAFS spectra do not reveal strong changes in the functional groups, we can conclude that the condensed species show in general similar chemical fingerprints as the fresh particles but with slightly increased carboxyl-C, alkyl-C or O-alkyl-C and less carbonyl-C.

Spectrum c) in Figure 5.5 shows an averaged spectrum of the fresh soot particles emitted from the EURO 2 transporter. A high absorption intensity at 285.2 eV can be observed. The steep increase at 292 eV and the absorption at 305 eV show the high degree of conjugation from large PAHs, graphene
5.4. Results and Discussion

Figure 5.7: Representation of the averaged single contributions of the fitted gauss integrals with their standard deviations. All spectra were normalized by the integral of the carbon edge spectrum from 280-320 eV. The black circles illustrate the soot particles from the wood stove, the blue squares the EURO 2 soot particles and the red triangles the EURO 3 soot particles. The solid and open symbols represent the unprocessed and aged soot particles, respectively.

and graphite type moieties. A weak absorption is found at around 288.3 eV that indicates a low degree of oxidization of the soot particles. The fitting analysis (Figure 5.7) shows strong particle to particle variability in the absorption intensities of the aromatic carbon, especially the absorption intensity at 292 eV. Again, the fitting analysis shows no evidence for phenol- or quinone-C absorption.

The aged particles depicted in spectrum d) of Figure 5.5 show a slightly higher aromatic content with an absorption feature at 305 eV. The ratio of the peak height at 285 divided by the peak height at 292 eV increases upon aging, from 0.63 to 0.72, indicating a decrease in alkyl-C, which is consistent with the AMS measurements [Chirico et al., 2010], and increase in unsaturated carbon, respectively. The carboxylic-C at 288.3 eV from the aged EURO 2 transporter particles shows the highest absorption intensity of all investigated particles. The fitting analysis confirms these observations. The AMS data support the analysis and show an increase of the mass fraction m/z 44. The fresh soot particles show a carboxyl carbon content of about 2.5 % of the total mass while in the aged particles a fraction of 5.4 % is observed. This increase in m/z 44 may be explained by the condensation of photo-chemically aged compounds. The organic mass was shown to increase by a factor of around 4 in this experiment due to formation of SOA. Therefore, we conclude that this increase in carboxylic-C in the NEXAFS spectra is mostly likely due to such organic compounds. Besides the strongly oxidized carbon compounds that condense on the soot particles, the aged particles show a high content of unsaturated and phenolic carbon which might also stem from polymerization and aldol type condensation reactions. Aldol condensation requires acidic conditions, but also ammonium salts and carbonate salts were shown to be efficient catalysts for similar aggregation reactions in atmospheric aerosols [Nozière et al., 2010]. Thus,
particulate phase aging processes may be the result of both the condensation of gas phase species and chemical processes initiated within the condensed phase [Zelenay et al., 2011b].

The averaged spectrum (Figure 5.5 e) of the unprocessed soot of the passenger car shows also a high absorption of the aromatic carbon at 285.2, as well as at 292 and 305 eV. Again, this points to a high graphitic content in these particles [Diaz and Hussain, 2007]. As already observed in the other fresh particles emitted from the transporter, the absorption intensity of the carboxyl-C is low and no phenol-C nor quinone-C absorption is observed. This is confirmed by the fitting analysis. The corresponding spectrum of the aged particles is shown in Figure 5.5 f). An increase in the absorption intensity of the carboxyl-C region is observed, which is also supported by the AMS measurements revealing an increase in the carboxyl content from 1.6 % in fresh soot particles to a content of 3.2 % in aged particles. This increase was accompanied by a comparably small increase in the aromatic-C at 285.2 and 292 eV in the NEXAFS spectra. The Gaussian fitting analysis, displayed in Figure 5.7, confirms the aforementioned changes. Note that the Gaussian fitting possibly exaggerates the absorption intensity at 292 eV, due to the uncertainty of placing the ionization edge properly, as mentioned above. The ratio of the peak height at 285 divided by the peak height at 292 eV shows a decrease from 0.76 to 0.72 upon aging, indicating an increase in alkyl-carbon groups. Additionally, it shows that no phenol-C and quinone-C evolved during the processing in the smog chamber. As in this case the AMS observed only a slight increase in organic mass by around 25 % from the starting concentration, we need to take into account that also primary soot particles might have been oxidized upon aging in the smog chamber and are jointly responsible for the observed changes in the NEXAFS spectrum. Therefore, the increase in carboxylic-C might also stem from primary particle oxidation and not from the oxidized organic compounds that condensed on the soot particle. The increase of the alkyl-C must have originated from condensed organic compounds as there is no other source available that could reasonably explain this increase.

Additionally, O to C ratios can be calculated by comparing the pre-edge (280 eV) and the post-edge absorption (320 eV) with the attenuation coefficients taken values from Chantler [Chantler, 1995] and assuming only carbon and oxygen being present in the soot particles. A ratio (and corresponding standard deviation) of 0.30 (±0.22) for fresh and 0.35 (±0.30) for aged wood combustion particles is found confirming only small additional incorporation of oxygen in the particles. Comparable values are revealed from AMS data, which showed a ratio of 0.35 for fresh wood combustion particles and a ratio of 0.40 for processed particles. Note, that only compounds that evaporate at 600 °C are measured with the AMS. The diesel combustion particles show a lower O/C ratio of 0.16 (±0.39) for fresh and 0.32 (±0.27) for the aged EURO 2 diesel exhaust particles. This is consistent with the addition of carboxyl-C and phenol-C in the particles as observed in the NEXAFS spectra. The AMS data reveal an O/C ratio of 0.1 for fresh and 0.34 for aged particles. Ratios of 0.12 (±0.13) for the fresh and 0.25 (±0.18) for aged par-
ticles emitted from the EURO 3 passenger car were found, consistent with AMS data (0.1 for fresh and 0.22 for processed particles). These values are consistent with the observation that less oxidized compounds condensed on the EURO 3 soot particles as observed for the EURO 2 car. Since the AMS only measures O/C ratios of non-refractory compounds the consistency between the NEXAFS derived O/C ratio and that derived from the AMS data is surprising. We therefore attribute a significant systematic uncertainty to our analysis. Nevertheless, it remains useful to discuss the relative changes.

### 5.4.3 Water uptake in soot particles

The water uptake behavior of the different soot particles was investigated via NEXAFS spectra measured at the oxygen edge and images measured at the oxygen edge and carbon pre-edge. The carbon NEXAFS analysis revealed a relatively low O/C ratio in most of the single soot particles. A NEXAFS analysis at the oxygen edge was impeded by the low oxygen content of the dry particles lead to low absorption and insufficient statistics for clear spectra. The O K-edge spectra reported below were measured for the aged wood stove sample at 0 % and 90 % RH and the fresh wood combustion particles at 90 % RH as well as for the aged soot from the EURO 2 transporter at 90 % RH. The spectra at the oxygen edge were only obtained from 2-3 particles, selected for having sufficient absorption at the oxygen edge and therefore may not be entirely representative.

Spectrum a) in Figure 5.8 shows the oxygen spectrum of unprocessed wood stove soot measured at 90 % RH. The main absorption is found at 538.2 eV, which is attributed to the transition of ketone-, carboxyl- or alcohol-O. A second absorption is found at around 532 eV. This absorption intensity is assigned to the O 1s→π* transition of carboxyl- and ketone-O [Hopkins et al., 2007]. Spectrum b) is from the aged soot sample from the wood stove at 0 % RH, which also displays a strong absorption peaks centered at 532 eV and 539 eV, and are attributed to the transitions of the aforementioned oxygenic functional groups. Spectrum c) is also from an aged wood combustion particle as b) but measured at 90 % RH. This spectrum strongly resembles that of liquid water [Tzvetkov et al., 2008, Cavalleri et al., 2002, Wernet et al., 2004]. Since water does not absorb at 532 eV, this peak is strongly diminished and indicates the dilution of the organic compounds [Myneni et al., 2002, Naslund et al., 2005, Wernet et al., 2004]. Figure 5.8 d) shows the spectrum of the EURO 2 transporter exhaust particles, measured at 90 % RH. The main absorption is found at 539 eV with a smaller transition at 532 eV. No signatures of water are apparent here. The main edge is similar to the dry spectrum of particles from wood combustion. Therefore, significant amounts of water were absorbed by the aged wood combustion particles, but not by the car exhaust particles. Interestingly, while potassium salts are expected to be associated with wood combustion particles and which can be expected to participate in water uptake, the characteristic potassium double peak near 300 eV was not observed in the C-edge spectra. The other spectra
shown in Figure 5.8 measured at high humidity also did not exhibit the typical features of water and so we conclude that the amount of water absorbed by the particles of these particular two soot samples was low, without formation of a substantial aqueous phase.

Figure 5.8: O K-edge NEXAFS spectra of a) fresh soot particles from the wood stove measured at 90 % RH, b) aged soot from wood stove at 0 % RH, c) same particles as in b) at 90 % RH, d) aged soot from the EURO 2 transporter at 90 % RH. The spectra are normalized to the highest absorption intensity.

Images of individual soot particles were recorded at different RH in order to quantify water uptake. As described above, the oxygen content was too low in certain soot particles, so that measurements at the oxygen edge were not possible in many cases. Therefore, the changes in the pre-edge region at the carbon edge were used to map the water uptake in particles with low oxygen content. The advantage here is that the particle positions are determined using the x-ray absorption at the carbon edge and hence there is no pre-selection bias towards oxygen content of the dry particles. Nevertheless, note that the contribution of oxygen to absorption at the carbon pre-edge remains small and therefore also the differences in absorption intensity at various RH. Therefore, criteria for detecting water uptake were defined, which include 1. a consistent change of the absorption intensity of the single particles with varying RH; this means that the absorption increased simultaneously with RH and vice versa, and 2. larger than 10 % difference in the absorption intensities of the single particle upon water uptake. No changes in the soot morphology were observed upon water uptake. The expected small changes upon restructuring are beyond the spatial resolving power of STXM as operated in the present experiments. The time steps in between the different RH settings were chosen to be at least 30 minutes before the
measurements were continued in order to allow the water uptake to reach equilibrium. Figure 5.9 shows the chemical map of one soot structure from an aged wood combustion particle at the oxygen edge at 0 %, 70 %, 93 % and returning to 0% RH again. At 70 % RH a first small change can be observed, which is manifested more clearly at 93 % RH. Very high uptake can be observed in some parts of the soot structure, which is colored in green and red. Here, an averaged water column of about 40 nm per image pixel is observed (assuming a density of 1 g/cm$^3$). In the other regions of the particle, an average water column of around 10 nm is observed. Returning again to 0 % RH, the absorption decreases to the initial values. From 16 investigated particles/structures, 11 were found to take up water. The unprocessed wood particles were also measured, but the absorption intensity was inconsistent during changes of RH and so the evaluation of these data has been omitted. The HTDMA measurements, shown in Figure 5.10, indicate a restructuring of the soot particles after exposure to 95 % RH. A GF of 0.95 was measured after six hours. Although a strong restructuring was observed indicating a compaction of the aged soot particles under high RH, after pre-humidification a GF of only 1.03 was measured (Figure 5.10), indicating little water uptake. Note that the HTDMA measures the electrical mobility diameter (equivalent diameter calculated from the mobility of the charged particles in the carrier gas). In contrast, the x-ray absorption measurements quantify the water uptake in terms of mass, which is a better indicator of water uptake in these particles.

Figure 5.9: Series of chemical maps showing the water uptake in aged wood soot particles, the images were measured at 543 eV. The images were recorded at the same position at different RH. The color bar represents the scale of the OD in the images.

Figure 5.11 shows the water uptake in a fresh particle of the EURO 2 transporter. These images were measured at the carbon pre-edge at 0 %, 80 %, 90 % and again at 0 % RH. The increase in absorption intensity can be already observed at 80 % with some additional increase in absorption at 90 % RH. After returning the RH to 0 %, the absorption intensity was observed in this case to not fully decrease to the initial level. This residual additional absorption could stem from either x-ray radiation damage or residual water trapped in the soot particle due to irreversible transformation of the soot particle during ‘swelling’ [Popovicheva et al., 2008]. However, we find an average water column of 15 nm in this soot particle at 90 % RH. The particle is calculated to have an average thickness of around 55 nm assuming a density of 1 cm$^3$/g for the dry carbon backbone. From the 10 investigated particles, 3 particles were found to take up water.
Figure 5.10: GF of wood combustion particles and soot particles from the EURO 2 transporter and EURO 3 passenger car measured with an HTDMA. Filled symbols illustrate the GF of 200 nm sized soot particles with a humidity pre-treatment.

Figure 5.11: Absorption maps of an individual unprocessed EURO 2 transporter combustion particle measured at 280 eV, at 0, 80, 90 and then returning again to 0 % RH.

The aged soot particles from the transporter were investigated at the pre-edge of the carbon edge and at the oxygen edge. Among 19 investigated particles, water uptake was observed in 12 particles. The aging in the smog chamber showed a shift from a low uptake capability of fresh soot particles to a higher uptake capability in aged particles. This increase in particle hygroscopicity was also measured with the HTDMA, see Figure 5.10. A GF of 1.02 was measured before processing of the soot particles and a GF of 1.04 was observed after 5 hours of processing (the observed GF increased further to 1.06 with pre-humidification).

Figure 5.12 shows an example of an unprocessed soot particle from the EURO 3 passenger car. This combustion particle was measured at 0 %, 85 % and returning to 0 % RH again. No significant change in x-ray absorbance was observed at any of the three RH levels. In other words, no water uptake was observed in any of the unprocessed EURO 3 exhaust particles investigated.

In half of the aged particles emitted from the passenger car, water associated within the particle was observed at 90 % RH, in agreement with the HTDMA measurements. While the fresh soot particles did not show any change in GF (GF ≈ 1.01), GFs of 0.96 and 1 without and with pre-humidification,
5.5. Conclusions

Figure 5.12: Absorption maps of a fresh EURO 3 passenger car soot particle measured before the carbon absorption edge at 280 eV at different RH.

respectively, were observed after processing in the smog chamber and a restructuring, caused by the condensation of oxidized compounds.

5.5 Conclusions

Single particle analysis was performed on fresh and aged wood combustion and diesel exhaust particles using scanning transmission x-ray spectro-microscopy and SEM analysis. The use of a custom reactor cell allowed in-situ exposure to varying relative humidity environments and hence the analysis of water uptake behavior in single particles. Two different cars, a EURO 2 transporter and a EURO 3 passenger car, and a wood stove were chosen as combustion sources. Aging of the particles was performed in a smog chamber. Analysis of the particle morphology reveals that all particles increased in size upon photochemical aging. Using NEXAFS spectroscopy, we found that in wood combustion particles the chemical fingerprints of unaged particles and oxidized compounds that condensed on the soot particles during photochemical aging are very similar, with only slightly increased carboxyl, alkyl or O-alkyl, and less carbonyl-C content. Aging of the particles from the EURO 2 car led to a higher content in unsaturated carbon as well as a higher content in phenols and carboxyl carbon, indicating that both condensation of oxidized species from the gas phase as well as particle phase chemical processes contributed to the composition of aged particles. The EURO 3 car particles revealed only small changes in the spectra upon photochemical aging due to either condensation from the gas phase or oxidation of primary soot. Furthermore, we showed that the water uptake behavior upon processing changed. We found that after processing the number of particles taking up water increased in accordance with HTDMA measurements. These changes can be directly related to the chemical fingerprints measured with NEXAFS. Therefore, the increased amount of carboxyls/phenols stemming either from direct oxidation of the soot particles or from condensation of organic compounds on the soot particles lead to higher water uptake ability of the particles.
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Bibliography


Chapter 6

UV/Vis radiation increases steady-state uptake of ozone on soot

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Chapter 6. UV/Vis radiation increases steady-state uptake of ozone on soot

6.1 Abstract

Oxidative aging of soot particles in the atmosphere may contribute significantly to their climate and human health effects. With their large specific surface area, soot particles are an ideal substrate for heterogeneous reactions. However, these reactions are typically of limited relevance due to deactivation of the surface. Here we show that light in the UV-A and visible range significantly enhances the reactivity of soot with ozone. In these laboratory experiments, soot from a propane burner was first ‘passivated’ with ozone (ozone mixing ratio of 300 ppb) for 15 hours before ozone uptake was measured in presence of UV radiation. Passivated soot was shown to be reactivated during irradiation with a four times higher steady state ozone uptake rate as compared to dark conditions. The uptake increased even by a factor of 15 when humidity (95 % RH) was introduced into the system. Possible mechanisms of ozone uptake are discussed. Further analysis using near edge x-ray absorption spectroscopy and contact angle measurements showed a decrease of oxygenated functional groups in the soot upon exposure to ozone and ozone in combination with light.

6.2 Introduction

The importance of soot particles in atmospheric chemistry and physics was assessed already in several studies [Ackerman et al., 2000, Bond and Bergstrom, 2006, Chameides and Bergin, 2002], with their role in health effects of particulate matter [Highwood and Kinnersley, 2006] and their significant effects on climate being of primary interest. Soot is the product of incomplete combustion processes and is generally composed of elemental (black) carbon and a range of other, partially also light absorbing compounds [Pöschl, 2005]. We explicitly include these additional organic compounds under the umbrella term soot in the present context.

The direct effect of soot particles on climate by absorbing radiation is supposed to be second strongest after CO₂ [Jacobson, 2001]. Depending on the hygroscopic properties, soot particles can also affect climate indirectly by acting as cloud condensation nuclei (CCN) [Koehler et al., 2009]. Early presumptions that soot with its large specific surface area may provide a substrate to catalyze ozone depletion have not been confirmed. Soot rapidly deactivates in the troposphere and its long term reactivity with ozone was shown to be too slow and thus unable to affect the gasphase ozone budget under dark conditions [Disselkamp et al., 2000, Lelievre et al., 2004, Pöschl et al., 2001]. The reaction with ozone still contributes to oxidative aging of soot particles in the atmosphere with potentially significant impacts on the fate of toxic species [Shiraiwa et al., 2011] or the hygroscopic and CCN properties [Koehler et al., 2009]. The main motivation of the present study was to assess whether the presence of tropospherically relevant UV/Vis light changes our current understanding of soot reactivity with ozone.
6.3 Experimental Section

Recently, photochemical processes have been shown to enhance uptake of gaseous oxidants on various surfaces. Experiments with titanium dioxide demonstrated that significant and sustained uptake of ozone was observed in presence of near UV radiation, with an uptake coefficient of $3 \times 10^{-5}$ [Nicolas et al., 2009]. Enhanced uptake of ozone under the effect of UV-A radiation at atmospherically relevant irradiance levels were observed on a number of different organic substrates, e.g., on benzophenone and benzophenone-phenol mixtures [Jammoul et al., 2008], on pyrene [Styler et al., 2009] and on humic acids [D’Anna et al., ]. Since soot with its significant fraction of associated organic carbon is significantly absorbing UV-Vis radiation, one might expect similar effects. Indeed, [Monge et al., 2010] presented results on NO$_2$ uptake over soot films in presence of artificial solar radiation. It was found that under irradiation, the NO$_2$ loss was enhanced and remained constant over several hours in contrast to measurements in the dark where the integrated NO$_2$ loss remained insignificant [Monge et al., 2010]. So far, the mechanism by which light enhances uptake of O$_3$ and other oxidants has not been entirely clarified but is likely due to direct photolysis processes and indirect processes via energy, electron or hydrogen transfer mediated by photoactivated intermediates.

In the present work, we studied the ozone uptake on soot surfaces by means of a coated wall flow tube technique. Significant ozone uptake was observed under UVA and Vis light on soot that had previously been passivated with ozone in the dark. Higher uptake coefficients were also observed at increased relative humidity (RH). Information about the evolution of carbon functional groups was obtained from offline x-ray absorption spectroscopy (XAS) experiments performed at the carbon K-edge, which provided some insight into potential reaction mechanisms. Finally, significant effects of light induced ozone uptake on the hydrophilicity were observed based on contact angle measurements.

6.3 Experimental Section

6.3.1 Coated wall flow tube experiment

A coated wall-flow-tube was used to determine the uptake coefficients. The soot was produced using a CAST (combustion aerosol standard) soot generator [Salgado and Rossi, 2002]. The soot samples were sampled, weighed and exposed to ozone within 24 hours. Propane (99.9999 %) was used as fuel (81 ml/min), and synthetic air as oxidant (1.52 l/min) and quenching gas (~30 l/min). A thin layer of soot was deposited in the inside wall of a Pyrex tube (inner diameter 0.6 cm, length 20 cm) by allowing exhaust gas from the exit of the soot generator to pass through the tube from both ends. The sampling temperature was between 35 and 55 °C. The soot mass was determined by weighing the Pyrex tube before and after coating. We did not attempt to weigh the tubes again after the coating to determine mass changes. Based on the results, these would have been too low. The evenness of the coating was
controlled by eye. Light absorption by the coated tube was very low and quantitatively comparable to that already used by D’Anna et al. [D’Anna et al., ]. For coatings as used also in that study NO₂ photolysis frequencies were measured under the exactly same geometric configuration. The resulting values were consistent with those calculated based on the actinic flux measurement outside the tube, indicating that absorption by glass, by the film and enhancement by scattering within the glass walls roughly cancel out mutually. The soot coated tube was then inserted into a horizontal cylindrical coated wall flow tube reactor with a total length of 60 cm. The coated tube was accompanied by two clean pyrex tubes upstream and downstream to ensure laminar flow over most of the length of the soot coated section. By circulating temperature controlled water through the cooling jacket of the reactor, the temperature was maintained at 293 K. Measurements with a radiation shielded thermocouple showed that the temperature changes in the gas flow were less than 1 K upon switching on lights. The reactor was surrounded by 7 sunlight lamps (Philips, 20 W) with a continuous emission from 300-420 nm and a total irradiance of 2.4·10¹⁶ photons cm⁻²s⁻¹. Visible radiation (400-750 nm) was generated with 7 lamps (Osram, 15 W) having a total irradiance of 4.4·10¹⁶ photons cm⁻²s⁻¹. All measurements were performed at atmospheric pressure. The flow rate in the coated wall flow tube was 770 ml/min using nitrogen as carrier gas. The RH was adjusted from 0 - 95 % and was controlled using capacity sensors. All flows were adjusted using mass flow controllers.

The ozone concentration was measured at the exit of the reactor using a photometric ozone analyzer (model ML 9810, Monitor Labs Inc, USA). Ozone was produced by irradiation of a diluted oxygen flow (7.7 ml/min oxygen, 100 ml/min N₂) at a wavelength of 185 nm using an ultra-violet lamp (Pen-Ray 3SC-9, UV Products Ltd., USA). The whole reactor could be bypassed which ensured no previous exposure of soot to ozone. A gas phase product analysis is not provided as no suitable instrument was available.

If not noted otherwise, soot was first exposed to ozone (300 ppb) during about 15 hours in the dark. After reaching a steady state, light was turned on until the ozone concentration reached a quasi steady-state. This took around 6 hours. After this time, the ozone concentration increased only very slowly further towards its initial value, i.e., uptake to soot decreased only very slowly. So it took e.g. additional 20 hours of exposure for the rate of ozone uptake becoming reduced by another 50 %. For comparison, the rate of uptake decreased by almost a factor of 7 from the moment of first exposure under irradiation until steady state. Results from a typical experiment are shown in Figure 6.1.

6.3.2 Determination of the uptake coefficient

Uptake coefficients were determined for the uptake of ozone in the dark (first exposure) and for the passivated soot under irradiation. To calculate the uptake coefficient a pseudo first order reaction is
assumed. The pseudo first order reaction coefficient ($k$) is related to the geometric uptake coefficient ($\gamma_{\text{geom}}$) by equation 6.1:

$$k = \frac{\gamma_{\text{geom}} \cdot \langle c \rangle}{2 \cdot r_{\text{tube}}}$$  \hspace{1cm} (6.1)

where $\langle c \rangle$ is the mean thermal velocity of ozone and $r_{\text{tube}}$ the flow tube radius. Additionally, the mass independent BET uptake coefficient ($\gamma_{\text{BET}}$) was calculated using equation 6.2:

$$\gamma_{\text{BET}} = \frac{S_{\text{geom}} \cdot \gamma_{\text{geom}}}{S_{\text{BET}} \cdot m_{\text{soot}}}$$  \hspace{1cm} (6.2)

with $S_{\text{geom}}$ the geometric area of the sample holder, $S_{\text{BET}}$ the specific BET (Brunauer, Emmett, Teller) surface area of soot and $m_{\text{soot}}$ the soot mass. The BET surface area of 137 m$^2$g$^{-1}$ was adopted from [Monge et al., 2010] because the same type of CAST burner and similar burning conditions were used. This BET surface is also comparable to the BET surface areas reported in other studies [Longfellow et al., 2000, Longfellow et al., 1999, Rogaski et al., 1997, Aubin and Abbatt, 2003, Lelievre et al., 2004, Al-Abadleh and Grassian, 2000]. Note that due to using very low soot sample masses to stay clearly in the mass independent kinetic regime, the total BET soot surface area in the coating was not by as much larger than the geometric surface area as it was the case in some other studies with soot. 

Due to the high depletion of ozone in many experiments, a correction for the diffusion in the gas phase was applied using the Cooney-Kim-Davis (CKD) method [Cooney et al., 1974] where the geometric uptake coefficient was evaluated to fit the experimental data. The implementation of this method is described elsewhere [Ammann et al., 2005]. Note that due to the relatively small flow tube diameter, the resulting corrections remained relatively small.
Uptake coefficients were determined at two different periods during an uptake experiment. Initial uptake coefficients $\gamma_{\text{initial}}$ and $\gamma'_{\text{initial}}$ (in the dark and for the passivated soot under irradiation, respectively) were evaluated from the average signal during the first 1.5 minutes. Steady state uptake coefficients $\gamma_{\text{ss}}$ and $\gamma'_{\text{ss}}$ (dark and irradiated passivated soot, respectively) were determined by averaging over 30 minutes starting after 15 hours in the dark and after 6 hours in the light. Note, that the term 'initial' here refers to the ozone loss averaged over an interval of the first 1.5 minutes. This is much longer than in traditional Knudsen cell or low pressure flow tube experiments coupled to much faster responding mass spectrometers, which allow initial uptake coefficients being determined in the millisecond range.

### 6.3.3 Characterization of the soot using x-ray absorption spectroscopy

Using XAS, namely in its Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy mode, chemical functional groups can be identified to support chemical characterization of complex mixtures [Stöhr, 1992].

The XAS measurements were performed at the Swiss Light Source (SLS) located at the Paul Scherrer Institut, Switzerland. This synchrotron radiation source operates at a beam energy of 2.4 GeV and electron current of 400 mA. The PolLux beamline [Raabe et al., 2008] possesses an energy resolution ($E/\Delta E$) of about 3000 within an energy range of 200-1200 eV well suited to perform NEXAFS spectroscopy at the carbon edge. The endstation is equipped with a focusing element, the zone plate, with a focus of about 40 nm. The intensity of the transmitted x-rays is measured using a photomultiplier tube (Hamamatsu 647P) [Tzvetkov et al., 2008] placed directly behind the sample. The spectra were measured in the stack mode, i.e., a series of images at closely spaced energy step sizes [Jacobsen et al., 2000]. The step size was chosen to be 0.2 eV in the range of 280-284 eV, 0.1 eV between 284.1-293 eV and 0.3 eV between 293.2-310 eV. The dwell time was set to 2 ms to minimize beam damage. The spectra were normalized according to the Lambert-Beer law $d \cdot \mu = -\ln(I/I_0)$, where $\mu$ is the mass absorption coefficient, $d$ the thickness of the sample, $I$ the transmitted light intensity across the sample, and $I_0$ the transmitted light intensity across the substrate. The energy calibration of the spectra was obtained by measurement of the well known transitions of polystyrene spheres [Dhez et al., 2003].

For the XAS analysis three soot samples were collected on a Si$_3$N$_4$ window by holding the window towards the exit of the CAST soot generator. Two soot samples were treated each one hour with 300 ppb of ozone and one of these was treated one additional hour with ozone under irradiation mimicking the conditions of the irradiated coated wall flow tube experiments. Note that in order to keep the same protocol for all three samples and the same time between treatment and analysis under the constraints of the beamtime at the SLS, the exposure time was shorter than in the flow tube experiments,
6.4 Results

but it should capture the main chemical changes in the soot particles for a qualitative comparison.

6.3.4 ESEM measurements

An FEI XL30, ESEM-FEG microscope with secondary electron detection was used in the wet mode with a beam voltage of 5 kV and a resolution of 2 nm. SEM measurements required sputter coating of the samples with gold prior to analysis. Soot was collected at the exit of the CAST burner on aluminum sheets until full surface coverage. These aluminum sheets were then exposed for 1 hour with 30 % RH to 2 ppm of ozone in the dark and under irradiation, respectively. In this case, the concentration was raised above that of the flow tube experiments to compensate for the shorter exposure time. For the irradiation, a Xenon lamp was used with a continuous emission in the range of 300-700 nm having a total irradiance of \(1.8 \times 10^{17}\) photons cm\(^{-2}\) s\(^{-1}\), which thus corresponds to combined UVA and Vis irradiation.

6.3.5 Contact angle measurements

Contact angle measurements were performed on soot samples using a computer controlled goniometric system (Digidrop contact angle meter, GBX). The soot sample treatment was equal to that performed for ESEM measurements.

6.4 Results

6.4.1 Ozone uptake experiments

Figure 6.1 shows the ozone concentration during first exposure to soot in the dark (black line) and then under irradiation (highlighted in yellow in Figure 6.1). In agreement with previous publications [Rogaski et al., 1997, Stephens et al., 1986, Lelievre et al., 2004], a large initial uptake could be observed during the first exposure of soot to ozone, followed by rapid surface deactivation [Lelievre et al., 2004] until almost complete passivation of the soot in the dark (Figure 6.1). Uptake coefficients calculated both based on the geometric surface area and based on the BET surface area are presented (Figure 6.2). Figure 6.2 shows a box plot of the measured uptake coefficients. The values for \(\gamma_{\text{initial}}\) are depicted in red, \(\gamma_{\text{ss}}\) in blue, \(\gamma'_{\text{initial}}\) in green and \(\gamma'_{\text{ss}}\) in black. Note that the uptake coefficient for irradiated conditions was determined using the loss of ozone from the difference of the steady state concentration at the end of the 15 hours dark period (\([O_3]_0\)) and the concentration measured under irradiated conditions. Therefore, more precisely, the \(\gamma'\) values represent only the reaction probability of ozone caused additionally by irradiation of the soot and not the total uptake.
Chapter 6. UV/Vis radiation increases steady-state uptake of ozone on soot

Figure 6.2: Box plot showing uptake coefficients (initial and steady state) of the dark and irradiated ozone depletion, the upper boxes represent the geometric uptake coefficients, the lower ones the BET surface area corrected uptake coefficients. The red boxes represent the initial uptake coefficients in the dark, the blue ones the quasi steady state after 15 hours in the dark, the green ones the initial uptake coefficient under irradiation after passivation in the dark and the black ones the quasi steady state uptake during irradiation. The number of experiments considered in boxes were 12 experiments for dark conditions and 13 experiments under irradiation. The whisker in the box plot represent the data range between 5 and 95 %.

The initial uptake coefficient was measured to be \((6.5 \pm 1.5) \times 10^{-5}\) based on the geometric surface area and \((1.26 \pm 0.3) \times 10^{-5}\) for BET surface area at about 300 ppb initial ozone concentration. After 15 hours of ozone exposure the uptake reached a quasi-steady state. This was found to be \((4.6 \pm 1.9) \times 10^{-7}\) and \((9.7 \pm 4.5) \times 10^{-8}\) for geometric surfaces and for BET surface areas, respectively.

After passivation of the soot, i.e., when the ozone concentration reached a quasi-steady state, lights were switched on. Again a high initial uptake was observed. \(\gamma'_{\text{initial}}\) was measured to be \((1.30 \pm 0.45) \times 10^{-5}\) and \((2.10 \pm 0.75) \times 10^{-6}\) for geometric and BET corrected surface area, respectively. This is less than one order of magnitude smaller than the initial uptake coefficient in the dark. Note again that only the influence of light was considered. A quasi-steady state was observed after a few hours. A steady state uptake, \(\gamma'_{\text{ss}}\), of \((1.9 \pm 0.44) \times 10^{-6}\) and \(3.6(\pm 1.36) \times 10^{-7}\) was measured for geometric and BET surfaces, respectively. These values are four times higher compared to the values measured under dark conditions. The main difference between the observed uptake under light to that in the dark, is this plateau of quasi-steady state uptake, which is sustained over long times. A recovery to the initial ozone concentration was never observed under irradiation (see also below). The uptake coefficients measured in the dark after 15 hours were close to the detection limit. The measured differences in the ozone signal, when uptake with light was measured, were always clearly above detection limits. Figure 6.3 shows the
measured uptake coefficients from an experiment over 2.5 days of irradiation. During this long period of irradiation the light was switched off a few times for a short period each to obtain a correct reference signal for the ozone depletion in the dark to take into account possible background shifts during the measurements. A BET uptake coefficient of \(8.34 \times 10^{-8}\) was measured after 36 hours and even after about 60 hours still an uptake of \(5.8 \times 10^{-8}\) was obtained. This finding, together with the observed ozone recovery when the light was switched off, suggests the formation of light induced intermediates able to react with ozone. Since the uptake coefficient continuously decreases over time, though slowly, the process seems not catalytic in its strict sense. The decrease with time may be driven by the consumption of light absorbing material, the sequential depletion of reactive compounds, the slow poisoning of catalytically active sites or by the physical exchange of absorbers or reactive intermediates by diffusion to the surface. The time dependence shown in Figure 6.3 is neither clearly representing a single exponential decay nor clearly characteristic of a bulk diffusion limited process that scales with \(\sqrt{D t}\), so that none of these mechanisms can be excluded. The dark uptake of ozone to soot was not investigated over such long time scale, since uptake was already close to the detection limit after 15 hours. Dark uptake coefficients measured by [Kamm et al., 1999] dropped to about \(10^{-7}\) over the course of a day.

![Figure 6.3](image)

**Figure 6.3:** BET surface corrected uptake coefficients measured under light over 2.5 days, the fit can be parameterized with \(\gamma_{\text{geom}} = 10^{-6.14} \cdot t^{-0.62}\).

Geometric and BET uptake coefficients on soot irradiated with visible light in the range of \(400-750\) nm were \(8.25 \times 10^{-7}\) and \(1.23 \times 10^{-7}\), respectively, a little more than a factor of two smaller than the uptake under UV irradiation. These results suggest that soot contains not only chromophoric material activated under UV but also material allowing activation under visible light. The difference in the uptake between visible light and UV scales very well with the difference in the absorption cross section of soot over this wavelength range [Schnaiter et al., 2003].
Experiments without previous passivation with ozone i.e., direct soot exposure to ozone, show the same steady state BET uptake coefficient \( (4.2 \times 10^{-7}) \) as \( \gamma_{ss}' \) measured with previously passivated soot. In contrast to this, the initial uptake coefficient shows a BET corrected uptake of \( 10^{-5} \), which is close to \( \gamma_{initial} \), the initial uptake coefficient measured in the dark. This suggests that the initial uptake of ozone was dominated by the reactions not affected by light and also ongoing on in the dark, while the steady state uptake, the one that is actually of relevance to the atmosphere, was dominated by the photochemical reactions.

The amount of ozone molecules depleted during 7.5 hours of UV irradiation (after previous passivation in the dark) depends linearly on the soot mass until a mass of about 3.75 mg (Figure 6.4). Therefore, all experiments were performed with soot masses below 3.75 mg. \( 1.13 \times 10^{17} \) ozone molecules were lost per mg of soot at 0 % RH during 7.5 hours within the linear range. Roughly 1 carbon out of 10'000 contributed to the destruction of ozone molecules when a non-catalytic reaction mechanism is assumed. Assuming that only surface molecules are involved, normalizing to the BET surface would yield \( 8.24 \times 10^{14} \) reaction sites per \( \text{cm}^{-2} \). This suggests that nearly each surface atom would be involved in depletion of ozone molecules.

![Figure 6.4: Number of ozone molecules depleted during 7.5 hours during irradiation; the line acts only as guide for the eye](image)

For dark conditions, the dependence of the uptake kinetics on the ozone mixing ratio is shown in Figure 6.5. An inverse dependence was observed as in previous studies, e.g. [McCabe and Abbatt, 2009]. This has often been described using a Langmuir-Hinshelwood type formalism. This mechanism involves first the adsorption of ozone on the soot surface before reaction. However, desorption of ozone in measurable amounts has never been observed, including this study. Interestingly, during irradiation a similar dependence was observed, although the dark and light induced processes seemed to be decoupled from each other based on the kinetic data. This might pro-
vide a hint that the rate limiting process, such as the formation of a first intermediate [Shiraiwa et al., 2011], may be similar for dark and light conditions. Based on a fit to the data shown in Figure 6.5, this dependence can be parameterized by $\gamma'_{geom} = 10^{-4.77} \cdot [O_3]_{initial}^{-0.42}$.

![Figure 6.5](image_url)

**Figure 6.5: Dependence of the uptake coefficients on the initial ozone concentration in the dark (black squares) and during irradiation (red triangles), the data points are fitted using the parametrization given in the text.**

Ozone uptake on soot was also investigated at different RH in the dark and under light. In the dark, soot was first passivated as described above, then the flow tube was bypassed and the RH changed. The ozone monitor was allowed to stabilize at the new humidity, which took several minutes. Afterwards, the gas mixture was again allowed to pass through the flow tube. In the dark, no significant dependence of ozone uptake on the humidity was found. This is in contrast to ozone uptake under irradiation, where a clear positive dependence was found (Figure 6.6). In this case, the soot was first passivated in the dark. After 15 hours lights were switched on and quasi-steady state uptake was allowed to establish. The lights were switched off and the RH was adjusted to the level of interest using the same protocol as described above. Then the lights were switched on until a new steady state was reached. Figure 6.6 shows that the uptake coefficient depends linearly on RH with $\gamma'_{geom} = 1.66 \cdot 10^{-6} + 5.66 \cdot 10^{-8} \cdot RH$ whereby the uptake coefficient at 95 % RH was about 3.5 times higher than at 0 % RH. The experiment was repeated with visible light. In this case the dependence was also positive with a linear dependence on RH, but the relative increase of the uptake coefficient was not as strong as under UV irradiation. The uptake at 80 % RH was two times higher than at 0 % RH.

A particularly interesting effect of the humidity was observed after the long term experiment as illustrated in Figure 6.3. As mentioned above, the soot showed still significant ozone uptake after about 60 hours of permanent irradiation under dry conditions. When the humidity was adjusted after this period to 74 % an 'initial' uptake of $10^{-5}$ (geom) and $1.38 \cdot 10^{-6}$ for BET corrected surface was observed at 300 ppb of ozone. After additional 12 hours exposure at 74 % RH, still an uptake of $2.1 \cdot 10^{-6}$ (geom) and $2.8 \cdot 10^{-7}$ (BET) was observed. Note that before this, the soot was passivated during 15 hours in the
dark, during 60 hours under irradiation and dry conditions and additional 12 hours to ozone, light and humidity. In addition, when finally humidification was switched off, an uptake of $1.37 \cdot 10^{-6}$ (geom), $1.87 \cdot 10^{-7}$ (BET) was measured at 0 % RH after additional 10 hours. This is still more than 3 times higher than after 60 hours without previous humidification.

Uptake measurements on soot without previous passivation were performed at different RH, i.e., the surface was directly exposed to ozone, humidity and light. The initial uptake coefficients were independent of RH, which is consistent with our observations in the dark. The steady state uptake coefficient showed the same positive dependence on the RH as the uptake coefficients measured after passivation.

The dependence of the uptake coefficient on the light intensity for two different RH values is shown in Figure 6.7. The observed linearity highlights the photochemical nature of our observations and allows an extrapolation to atmospheric conditions [D’Anna et al., ]. The photon intensity in the troposphere in the wavelength range of 300-400 nm is expected to be $1.9 \cdot 10^{16}$ photons cm$^{-2}$s$^{-1}$ at a solar zenith angle of 48.19° [Gueymard et al., 2002, D’Anna et al., ]. Using the linear relationship of Figure 6.7 one can scale the uptake coefficient to atmospheric conditions taking 30 ppb as initial ozone concentration and 0 % RH. This would suggest an uptake coefficient of $4.5 \cdot 10^{-6}$ for the geometric surface area and $7.2 \cdot 10^{-7}$ corrected for the BET surface area. The red open data points in Figure 6.7 illustrate the light dependence at 84 % RH. Possible reaction mechanisms under different RH are discussed below.

An additional experiment was performed with semivolatile material from the CAST generator. The sampling procedure was the same as described for the soot sampling, but the solid particles from the exhaust were filtered before sampling. Here the sampling time was comparable to other experiments, i.e. around 10 minutes. The temperature of the filter was not stabilized at a certain value, but due to the high quenching flow the temperature decreased rapidly so that it was below 40 °C. The material deposited was not visible by eye. The first exposure to ozone showed again a high initial uptake with a geometric uptake coefficient $\gamma_{\text{initial}}$, which is comparable to the uptake coefficients measured for soot
6.4. Results

Figure 6.7: Steady state uptake coefficient as function of irradiance (7 lamps having a total irradiance of $2.4 \times 10^{16}$ photons per cm$^2$ and s) measured at 300 ppb of ozone, black data points were measured at 0 % RH, the open red data points were measured at 84 % RH.

(i.e. $1.3 \times 10^{-4}$). But full recovery of the ozone concentration was occurring within a few minutes so that $\gamma_{ss}$ was below the detection limit. Nevertheless, the passivation was continued for 15 hours before the lights were switched on to make it comparable to the soot experiments. The initial uptake under irradiation was comparable to the experiment with soot, i.e. $\gamma'_{\text{initial}} = 1.16 \times 10^{-5}$ and the quasi steady state uptake $\gamma_{ss} = 10^{-6}$ only slightly lower than for the experiments measured with soot particles. This rather qualitative experiment shows that the semivolatile material present in the exhaust shows comparable reactivity as the deposited soot (containing the semivolatiles presumably condensed on the soot particle surface). It could provide a hint that the key species involved in the photochemical processes might even be among the semivolatile organic fraction of soot. We expected that such semivolatile compounds may have evaporated from the soot coated section of the flow tube. Therefore, a few experiments were also performed at 10 C$^\circ$, but no significant increase in ozone uptake was found. This test for the effect of evaporation under the conditions of the standard experiments is not entirely conclusive, since evaporated material may have reacted with ozone on the surface of the uncoated tube section further downstream still in the irradiated region of the photoreactor.

6.4.2 NEXAFS spectra of CAST soot and ESEM measurements

X-ray absorption spectra of CAST soot were measured at the carbon edge, where different chemical functionalities can be identified as e.g. unsaturated carbon (285 eV), ketones/phenols (286.7 eV), aliphatic/aromatic carbon (287.4-287.7 eV), carboxyls (288.2-288.6 eV), alcohol/ carbonyl/ O-alkyl-C (289.3 eV) and the 1s transition to $\sigma^\ast_{C\cdots C\cdots O\cdots C\cdots C}$ (292 eV) [Braun et al., 2006, Diaz et al., 2001, Stöhr, 1992, Haberstroh et al., 2006, Hopkins et al., 2007]. Note that between 286 and 291 eV all peaks stem from resonant transitions in oxidized carbon apart from the peak region around 287.5 eV [Hopkins et al., 2007]. Figure 6.8 shows average spectra obtained from the three differently treated soot samples:
untreated soot (lower spectrum), soot exposed during one hour to 300 ppb ozone (middle), and soot exposed during one additional hour to the same concentration of ozone under irradiation (upper spectrum), respectively. The spectra were averaged from 6-11 individual particles with a diameter of about 300-500 nm. The spectra were normalized to the absorption at 315 eV. The grey bars show the important absorption intensities (unsaturated carbon, saturated carbon, carboxylic carbon, O-alkyl carbon and the 1s transition to $\sigma^\ast_{C-C, C-O, C=O}$).

Slight variations in the absorption intensities can be observed upon soot aging. In the region of unsaturated carbon at 285 eV all three samples show a high absorption intensity that remains constant during all treatments. In contrast to this, absorption in the aromatic/aliphatic region at around 287.5 eV decreases for the combined exposure of the sample to ozone and light. In the region around 288.2 eV, where carboxyl carbon absorbs, the untreated (fresh) and ozone treated soot show a higher absorption than the soot treated with ozone and light. At 289.3 eV, the absorption region of O-alkyl carbon, the absorption intensity of soot decreases upon exposure to ozone solely and remains low also upon exposure to light and ozone. At around 292 eV, the absorption of $\sigma^\ast_{C-C, C-O, C=O}$, ozone exposure in the dark leads to a reduction in absorption intensity, while exposure to light does not lead to further changes. A broad feature at 305 eV caused by $\pi$ conjugation becomes more apparent upon exposure of
soot to light and ozone. The evolution of this peak has also been observed when amorphous carbon is annealed at high temperature [Díaz et al., 1999].

To study possible changes in the morphology of the CAST soot samples due to ozone and light treatment ESEM images were recorded. Figure 6.9 shows the freshly emitted soot (left), the ozone treated soot (center) and the soot exposed to ozone under irradiation (right). Consistent with other authors, e.g. [Daly and Horn, 2009], chain-like aggregates of primary soot particles are observed. These particles showed sizes of $37 \pm 13$ nm. Although the particles appear to be slightly less amorphous and more like spherule clusters after the treatment, no significant changes in the morphology seemed to occur.

![Figure 6.9: ESEM images of fresh CAST soot (left), soot after ozone exposure in the dark (center) and soot after ozone-light treatment (right).](image)

### 6.4.3 Contact angle measurements of CAST soot

Figure 6.10 shows images from the contact angle measurements of the soot upon different treatments. To ensure a homogeneous soot coverage on the aluminum sheets, different sample locations were investigated, which showed all the same contact angle. Figure 6.10a shows the water droplet on untreated soot. A contact angle of $80 \pm 3$° was measured. Figure 6.10b shows the water droplet on the soot after exposure to 2 ppm of ozone for 1 hour at 30% RH. The wettability of the ozone treated soot is already significantly reduced which is demonstrated by an increase of the contact angle to $100 \pm 4$°. Figure c) shows the water droplet on soot upon the combined exposure to light and ozone at 30% RH. Here, the wettability of the soot was even worse whereby the contact angle increased to $120 \pm 3$°. This strong increase in contact angle is surprising and may parallel the reduction in oxidized carbon functional groups observed in the NEXAFS analysis.
Chapter 6. UV/Vis radiation increases steady-state uptake of ozone on soot

Figure 6.10: Contact angle measurements of the differently treated soot samples deposited on aluminum sheets, a) shows the water droplet on untreated soot with a contact angle of 80°, b) the water droplet on soot after exposure to 2 ppm ozone at 30 % RH showing a contact angle of 100°, and c) the droplet on soot after exposure to light and ozone at 30 % RH with the highest contact angle (120°)

6.5 Discussion and comparison to literature

6.5.1 Uptake coefficients in the dark

The comparison of the measured uptake coefficients (BET corrected: $1.26 \times 10^{-5}$, geometric surface area: $6.5 \times 10^{-5}$) with literature values shows that $\gamma_{\text{initial}}$ for BET corrected surfaces falls grossly into the range of uptake coefficients reported for BET corrected uptake coefficients in the literature ranging from $10^{-3}$ measured in an aerosol chamber (Degussa carbon black) [Disselkamp et al., 2000], over $(3.8 \pm 1.4) \times 10^{-4}$ for toluene soot measured in a coated wall flow tube [Lelievre et al., 2004], to $(0.08-1) \times 10^{-3}$ for hexane soot also measured in a flow tube [McCabe and Abbatt, 2009] (no time scales provided). We emphasize that this comparison is somewhat problematic, because the term ‘initial’ refers to different response times of the different experiments. In our experiments, $\gamma_{\text{initial}}$ is the average over the response time in the order of 90 sec, which is also sufficient for O$_3$ to explore the full BET surface area. In other, faster responding experiments, this is not necessarily the case. This might be the reason why our values lie at the lower end of the range established in the literature. For the same reason, the values for $\gamma_{\text{initial}}$ calculated with the geometric surface area may be low compared to the values in the literature, which are $7 \times 10^{-2}$ for methane soot measured in flow tubes [Longfellow et al., 2000] and $10^{-3}$ for Degussa carbon black measured in a Knudsen cell [Rogaski et al., 1997]. Again, a more detailed analysis of other data sets would be necessary to compare them directly in terms of average uptake coefficients integrated over comparable time intervals [Ammann and Pöschl, 2007].

The BET corrected quasi-steady state uptake coefficients ($\gamma_{\text{ss}}$) of $9.8 \times 10^{-8}$ measured with CAST soot in this study lie within the range of uptake coefficients reported in the literature e.g., $(2.7 - 11.3) \times 10^{-5}$ for charcoal [Stephens et al., 1986], $10^{-8}$ for Degussa carbon black [Disselkamp et al., 2000] or $8 \times 10^{-5}$ for methane soot [Longfellow et al., 2000]. The values are also well comparable to the values of Kamm et al. who reported an uptake coefficient of $(1.0 \pm 0.6) \times 10^{-7}$ at 296 K from an experiment in a large aerosol chamber [Kamm et al., 1999].

The kinetics and possible reaction mechanisms taking place in the dark will be only shortly discussed.
here. Suddenly stopping the admission of ozone to the flow tube resulted in a drop of the ozone concentration to the detection limit within the response time of the instrument. Apparently, no desorption of measurable amounts of ozone from the soot surface was taking place. Similar to Lelievre et al. [Lelievre et al., 2004], we infer an overall irreversible depletion of ozone at the soot surface. The negative dependence of the uptake coefficient on the ozone concentration is comparable to many other studies with soot but also with individual organic compounds or other substrates [McCabe and Abbatt, 2009]. McCabe et al. [McCabe and Abbatt, 2009] suggested that the kinetic behavior could be well explained by a non-catalytic Langmuir-Hinshelwood surface reaction, even though the similarity of the related parameters for vastly different substrates remained unexplained. Such a mechanism was able to explain different data sets covering different time scales in a consistent way by Ammann et al. [Ammann and Pöschl, 2007]. If the surface coverage of weakly adsorbed ozone is low and desorption of these adsorbed molecules is very fast, it would likely not have been detectable under our experimental conditions. Shiraiwa et al. [Shiraiwa et al., 2011] have recently suggested a more complex mechanism involving a relatively long-lived reactive intermediate playing a key role in the reactivity of soot and potentially other substrates with ozone.

A small uptake even after 15 hours in the dark could be measured here. One might be tempted to suggest a slow catalytic decomposition from this, as done so by Lelievre et al. [Lelievre et al., 2004] and Kamm et al. [Kamm et al., 1999]. The simulations of the Kamm et al. data presented by [Ammann and Pöschl, 2007] suggest that the remaining reactivity after long times might be explained by a slow self reaction of adsorbed O$_3$. Therefore, a detailed analysis of a data set covering a wider parameter space would be required to explore these mechanistic details in the dark.

### 6.5.2 Uptake under irradiation

The uptake coefficients for ozone on passivated soot under irradiation cannot be compared, because, to the best of the authors knowledge, no comparable ozone uptake experiments under irradiation have been reported in the literature. The dependence of the uptake coefficient on the irradiance clearly establishes the photochemical nature of the processes driving ozone uptake. The fact that the effects are more pronounced under 300-400 nm light than in the visible above 400 nm is consistent with the wavelength dependence of the mass absorption coefficient of many organic compounds potentially acting as primary absorbers. The most prominent organic compounds, the absorption spectrum of which extends significantly above 300 nm, are large polyaromatic compounds (PAH) and smaller poly- and mono-aromatic carbonyls and carboxyls [Keller-Rudek and Moortgat, 2010]. Many representatives of these have been identified in soot or as semivolatile species in combustion exhaust gases [Fraser et al., 1998, Miracolo et al., 2010, Schauer et al., 1999]. Especially aromatic ketones are known to be
actively involved in photoinduced reaction mechanisms, e.g. by driving photosensitized redox processes [Canonica et al., 1995] or by enhancing the degradation of PAH [McDow et al., 1995]. Other highly functionalized organic compounds, such as α-dicarbonyls are also known to absorb above 300 nm and undergo decarboxylation or induce polymerization [Guzman et al., 2006]. The involvement of smaller organic compounds associated with soot rather than the refractory, elemental carbon fraction of soot would also be consistent with the fact that photochemically reactive species seemed to be present in the condensate of filtered exhaust gas.

### 6.5.3 Mechanistic insights from NEXAFS spectra

As described in the previous section, lower absorption intensity was observed in the region of O-alkyl/alkyl- carbon upon exposure of soot to ozone in the dark. In this context it is important to remember that apart from the refractory part, soot consists also of organic material with a wide range of volatility, which condense on the more refractory primary particles during cooling in the exhaust line and after dilution and emission. The potential role of semivolatile exhaust species in the light induced ozone uptake is also a reminder of this. We suspect that many of these partially oxidized compounds are (further) oxidized, cracked and removed from the soot as already observed by Smith et al. [Smith and Chughtai, 1997], who found water and CO$_2$ as products of soot exposed to ozone in the dark. Gomez et al. [Gomez et al., 2006] and Net et al. [Net et al., 2010] observed the formation of small oxygenated organic compounds like formaldehyde from the ozonolysis of undecylenic acid and 4-phenoxyphenol, respectively.

The soot aged under ozone and light shows a decrease in the region at about 288.2 eV, where carboxyl carbon absorbs, thus suggesting decarboxylation. This is in agreement with the finding of Smith et al. [Smith and Chughtai, 1997], who studied the product formation upon uptake of ozone (15.3 ppm) to soot (15 mg) during sunlight irradiation (about 530-2050 nm) and showed a change of the product distribution towards H$_2$O, CO, and CO$_2$.

Parallel to this, the NEXAFS spectra indicate an 'increase' in π conjugation relative to the untreated soot supporting the idea that mainly the refractory part of soot, which consist of coupled polyaromatic, graphene and graphite type moieties, remained after ozone and light treatment. Also the contact angle measurements are consistent with the NEXAFS analysis. The resulting soot surface is less oxidized and thus less wettable than that before reaction. Overall, the measurements indicate quite vigorous oxidation chemistry.

In the literature, only few studies reported on the effect of light on the reaction mechanisms of ozone with condensed organic compounds. The reaction mechanisms include the quenching of the triplet state of benzophenone by oxygen through energy transfer, which was suggested by Jammoul et al.
6.5. Discussion and comparison to literature

[Jammoul et al., 2008]. The resulting excited states of oxygen are quenched by gas phase molecules or the organic film leading to its oxidation. For pyrene, Styler et al. [Styler et al., 2009] suggested that on the one hand the excited-state pyrene may react with oxygen to form \( \text{O}_2(^1\Sigma^+_{g}) \), which may then react with ozone to form \( \text{O}(^3\text{P}) \). \( \text{O}(^3\text{P}) \) may further react with oxygen to reform ozone or it may form oxygen when reacting with ozone. On the other hand, a charge-transfer complex with adsorbed ozone may be formed and photoexcited ozone may then dissociate to oxygenated pyrene radical and molecular oxygen. Besides energy transfer and charge transfer complex reactions also direct hydrogen and electron transfer have been suggested. From product analysis of mixtures of 4-phenoxyphenol and 4-carboxybenzophenone adsorbed on silica gel and supported by \( \text{ab-initio} \) calculations Net et al. [Net et al., 2009, Net et al., 2010] suggest that proton and electron transfer may occur between 4-carboxybenzophenone and 4-phenoxyphenol rather than energy transfer. The net effect of these processes is that absorption of light may strongly enhance the oxidative effect of ozone. This is also corroborated by the much larger integrated ozone depletion potential of soot under light than in the dark described above.

The observation that upon exposure to ozone and light the remaining soot is less hydrophilic and probably less oxidized, is in some contrast to other measurements that observe an increase in the amount of oxidized carbon compounds associated with soot [Smith et al., 1988, Koeber et al., 1999]. However, we note that the combined action of ozone and light, which has not been systematically explored before, leads to more vigorous oxidation chemistry through the scenarios discussed above.

6.5.4 Possible reaction mechanisms at high RH

Based on our results, humidity does not seem to influence the uptake kinetics of ozone in the dark. In contrast, the experiments reveal an enhancing role of the humidity on the ozone uptake during irradiation. Additionally, as described above, higher uptake was observed during the long term experiment after additional admission of humidity into the system. It seems that the humidity promotes the formation of photochemically active compounds or their physical exchange and exposure to ozone. Possible reaction mechanisms could be similar to the ones observed on dry surfaces via electron, energy or proton transfer, or charge transfer complexes [Canonica et al., 1995, Grgic et al., 2010, Styler et al., 2009]. In addition, for the reactions mentioned for dry conditions, the humidity may shift the reaction equilibrium by e.g. stabilization of intermediates.

In contrast to our measurements on soot, Jammoul et al. [Jammoul et al., 2008] suggested that competitive adsorption of water on benzophenone explains the negative dependence on humidity under irradiation. Competitive adsorption of water and ozone molecules and the quenching activity were suggested to be responsible for similar behavior on humic acids [D’Anna et al., ] and pyrene [Styler
et al., 2009]. Similar to our study Kamens et al. [Kamens et al., 1988] found an increased PAH degradation with increased humidity in an outdoor chamber exposed to natural sunlight. They assume that direct PAH photolysis, singlet oxygen oxidation and OH· attacks might be involved in the degradation. They explained the dependence on humidity with the formation of a water layer, which may exhibit an increased acceptance for reactive species like OH·. McDow et al. found an increased degradation of benz[a]anthracene and benzo[k]fluoranthene at higher humidity but not so for benzo[a]pyrene, which they ascribed to a shift of the absorption spectra of the PAH upon hydration, increased oxygen solubility, an increased lifetime of the triplet states or an increased stability of polar reaction intermediates. Increased degradation rates of organic compounds, e.g. phenols, in presence of UV [Kusic et al., 2006] and artificial solar radiation [Sanchez et al., 2003] were also found in aqueous solutions. We may also suggest a phenol-quinone coupled oxidation and reduction mechanism. Phenols may be oxidized to quinones when exposed to light and ozone [Mvula and von Sonntag, 2003]. Quinones in turn may be reduced back to phenols in an irradiated solution [Lente and Espenson, 2004], thus offering a photocatalytic cycle.

### 6.6 Conclusions

This study focused on the light enhanced uptake of ozone on soot. It was shown that after passivation of soot with ozone in the dark,  $\gamma_{\text{ss}}$ experienced a four fold increase in presence of UV radiation. Long term experiments, which lasted over 2.5 days under irradiation, showed still an uptake coefficient of $5.8 \times 10^{-8}$ under dry conditions. This uptake coefficient could be increased when humidity was temporarily introduced into the system. The long term behavior did not provide clear evidence about the rate limiting process, namely whether the long-term uptake is limited by physical processes, such as slow exchange of reactants with the bulk phase, or by chemical processes, such as depletion or poisoning of catalytically active sites. The dependence of the steady state uptake coefficient under light after about 6 hours on the ozone mixing ratio indicate a Langmuir-Hinshelwood type, surface-mediated reaction, comparable to the kinetics observed in the dark. The initial uptake of ozone upon exposure of fresh soot to ozone was found to be similar, independent of the conditions i.e. the presence of light or RH. This is in contrast to the quasi-steady-state uptake, which showed a positive dependence on RH during ozone uptake under irradiation. An increase by a factor of 3.5 was observed from dry conditions to 95 % RH. In the dark, no dependence was observed on RH. The analysis of the NEXAFS spectra of differently treated soot particles revealed decarboxylation and an increase in the degree of conjugation and intermolecular interactions between conjugated carbon systems upon exposure to ozone and radiation. This indicates that light and ozone in combination leads to much more vigorous condensed
phase oxidation mediated by radicals that would not be active under dark ozonolysis conditions. This leads to removal of organic carbon by oxidation and volatilization, leaving behind the more refractory fraction of soot. The contact angle measurements, where an increase in hydrophobicity was measured, support these observations.

6.7 Atmospheric implications

We could show that the influence of light prevents the complete deactivation of soot by ozone. Nevertheless, the ozone depletion potential remains negligible with respect to influencing the ozone levels in the atmosphere. Even if high urban soot loadings (30 µg/m$^3$) [Jacobson, 2001] are assumed, the change in the ozone concentration (1 mg soot depletes $10^{17}$ molecules of ozone during 7 hours (Figure 6.4)) is about 1.2 ppb at 0 % RH, which is insignificant. Based on fits to the dependence of the uptake coefficient on time, concentration and humidity as presented in Figures 3, 5, and 6, and assuming a linear dependence on RH at all concentrations, we suggest the following parameterization for inclusion in model calculations for mid-latitude lower tropospheric daylight conditions:

$$
\gamma_{BET} = \frac{(8.1 \times 10^{-8} + 2.76 \times 10^{-9} \cdot RH) \cdot t^{-0.62}}{[O_3]_{initial}}.
$$

For instance, this leads to an uptake coefficient of $5.44 \times 10^{-7}$ at 60 % RH and 30 ppb.

While hardly affecting the gas phase, the light induced reactions of ozone have a significant impact on aging of soot. The results suggest that the combined action of ozone and light leads to radical induced oxidation cycles likely involving polymerization and volatilization, so that the particles remain with their more refractory and less hygroscopic components. This may negatively influence the CCN ability of soot and thus extend its life time. The light absorbing, non-refractory fraction of soot is likely to affect also the photochemistry in internally mixed particles formed by condensation of other material or coagulation with other organic or inorganic particles. While the presence of an aqueous phase formed after deposition of soluble species to the soot surface may lead to quenching of excited species, it may also accept radicals to allow oxidation processes otherwise not expected there.

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Bibliography


Summary and Outlook

Summary

Key aspect in this work was to use a microspectroscopy approach to characterize the water uptake behavior in individual (sub)micrometer sized particles and link it to their chemical composition. This work improves our understanding of the interplay between morphology and hygroscopic properties as a basis for future assessments of optical and other essential parameters of aerosol particles. For characterization, x-ray absorption spectroscopy was used, which allows analysis of the functional groups in the particles. To enable morphological investigations and single submicron particle analysis, the scanning transmission x-ray microscope at the PolLux beamline located at the Swiss Light Source was used. In combination with x-ray absorption spectroscopy, hence microspectroscopy, it allows chemical characterization at a spatial resolution of 40 nm. In situ observations of water uptake in the single particles was performed in the microreactor, which we developed for these purposes, see also chapter 2. The microreactor allows to control the temperature, gas phase environment and pressure during the measurements so that in situ changes can be observed upon variations by one of these parameters. Different materials were chosen for the water uptake experiments such as ammonium sulfate, tannic acid and compound mixtures like ammonium sulfate/adipic acid, fulvic acid and soot. These compounds are either relevant in the atmosphere or they represent atmospherically relevant proxy compounds.

First results on the water uptake in single submicron particles are presented in chapter 3. Ammonium sulfate was chosen as test case to investigate the reliability of our system, as its hygroscopic properties are well known. By measuring the absorption intensity and size of single particles we could show that water uptake and release can be reliably mapped. Furthermore, the x-ray absorption spectra of ammonium sulfate and its saturated and supersaturated solutions were measured. Using the integrated spectroscopic features measured between 538 and 545 eV, the intensity of which was found to be specific for the associated water, it was possible to reconstruct the well known humidogram of ammonium
sulfate.
The morphology of mixed adipic acid/ammonium sulfate particles was investigated at RH < 2 % and 95 % RH. In both cases an inhomogeneous mixture of the two compounds was observed. At high RH, the ammonium sulfate deliquesced and was found to coexist with a structure containing likely undissolved adipic acid. It could not be resolved if the adipic acid forms a structure consisting of veins and pores filled with ammonium sulfate, that was indirectly inferred by others based on behavior observed with aerosol ensemble methods.

Water uptake behavior was also investigated in tannic acid and the Suwannee River fulvic acid, to represent a well known complex mixture of highly oxidized organic compounds that might have similarities with organic matter in atmospheric particles, see chapter 4. In both substances a continuous water uptake was found. In bulk fulvic acid samples, water uptake was found to result in a morphological separation of compounds showing different water uptake ability driven by differences in their functional groups. Carboxylic-rich compounds in fulvic acids were found to increase the water uptake ability while O-substituted aromatic groups suppressed the water uptake. The highest water uptake ability showed structures with high carboxyl-, O-alkyl- and carbonyl-C content. The separation induced by water uptake resulted in different morphologies. Large (several μm), optical dense O-substituted aromatic carbon structures were found. Such compounds were also found to evolve into smaller structures with sizes of only several hundreds nanometers. These structures were found to be embedded in a carboxylic/aromatic-rich solution.

To observe changes in water uptake behavior upon atmospherically relevant photochemical aging, single soot particles were analyzed, see chapter 5. Soot particles emitted from two different cars, a EURO 2 transporter and a EURO 3 passenger car equipped with an exhaust aftertreatment device, and a wood stove were investigated. Our results were compared with measurements of an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer and a Hygroscopicity Tandem Differential Mobility Analyzer. The exhaust, including the gas and the solid phase, was transferred to a smog chamber where the photochemical aging process was started. Freshly emitted as well as aged particles were collected and analyzed using x-ray absorption spectroscopy. The spectra of the single particles were decomposed using Gauss fits so that single transitions of the different functional groups could be quantified. We could show that the condensed species in photochemically aged wood combustion particles show in general similar chemical fingerprints as the fresh particles but with slightly increased carboxyl-C, alkyl-C or O-alkyl-C and less carbonyl-C. In contrast, the EURO 2 car showed an increase in carboxylic-C in the NEXAFS spectra which presumably stem from oxidized organic compounds condensing onto the particles during photochemical aging. These condensed organic compounds show also a high content in unsaturated carbon as well as high amounts of phenolic-C which might stem from polymerization and aldol type condensation reactions. In the EURO 3 combustion particles only a small increase in the
organic carbon was measured by AMS, therefore the observed changes like the increase in carboxylic-C might also stem from primary particle oxidation and not from the oxidized organic compounds that condensed on the soot particle. However, the increase of the alkyl-C, which was found in aged particles, stems presumably from organic compounds condensed onto the particles after gas phase oxidation. Separate aging experiments were conducted with laboratory generated soot. Coated wall flow tube experiments were conducted to elucidate the ozone uptake on soot in absence of other volatile exhaust gases. Hereby we could observe a photoenhanced uptake of ozone in soot. The uptake coefficient increased by a factor of four during irradiation and by a factor of fifteen when humidity was introduced into the system. Interestingly, the NEXAFS analysis revealed that the soot particles remained with their more refractory and less hygroscopic components after ozone exposure under irradiation, so that radical induced oxidation cycles likely involving polymerization and volatilization is assumed. The detailed discussion is found in chapter 6.

**Outlook**

The microreactor enables to define the gas phase environment of deposited submicron particles. In combination with microspectroscopy studies, it is a powerful tool to study changes in morphology and chemical composition, which might evolve upon variations in the gas phase. In this work water uptake behavior was studied. Future experiments are planned with reactive trace gases such as ozone so that e.g. oxidation can be mapped using specific absorption intensities in single particles. A possible system is oleic acid where the decrease of the intensity of the unsaturated carbon functional group due to double bond oxidation could be observed. The imaging method could reveal spatially resolved oxidation of oleic acid in e.g. a matrix compound. Finally, the microreactor should be further developed to simulate realistic atmospheric gas environments. This would enable to map the single particles and reproduce their aging in the atmosphere. Such knowledge could help to assess the lifetime of the aerosol particles in the atmospheres but also it could be useful to model the scattering/absorption properties of the aerosols dependent on their residence time in the atmosphere. The setup, as used in this work, allows for the first time to measure NEXAFS spectra at well defined relative humidity, temperature and pressure for single micron and submicron sized particles. This opens a broad field of possible investigations in the context of environmental sciences. E.g. ice with salt impurities can be now studied in the microreactor, but also hydrate phases of salts could be investigated. Additionally to our measurements, plenty of other experiments are conceivable. The measured data set could be enlarged with additional experiments on e.g. the water uptake behavior of well defined compound mixtures. It would be worth to compare our data set of ammonium sulfate/adipic acid with other organic/inorganic mixtures as e.g. ammonium sulfate/glutaric acid and investigate their mor-
phology as there is still a discussion ongoing how the morphology of dry multicomponent mixtures looks like after nucleation. One kind of morphology was predicted having a shell of eutonic composition surrounding a pure core of the compound, which is present in excess. Discussed are also homogeneous nucleation of all components or pure shells with mixed cores. As deliquescence depends on the morphology of an individual particle, such studies could help to understand the interplay of particle morphology and water uptake. Since the relationship between morphology and optical parameters are the topic of intense current research and debate, morphology information as obtained in the present study with STXM may be combined in the future with scattering/absorption studies, e.g. cavity ring down spectrometry, to model and explain the light interaction with aerosol particles.

Suwannee River fulvic acid revealed separation of compounds showing different water uptake ability depending on their functional groups. The morphology of fulvic acid is strongly influenced by the experimental conditions, i.e. pH, fulvic acid concentration and ionic strength of the initial solution. E.g. it was shown that the fulvic acids formed globular aggregates and ringlike structures at low pH and high NaCl concentrations, whereas small aggregates were formed at high pH. Therefore, further experiments should be conducted with different fulvic acid solutions to elucidate the effect of the aforementioned parameters on the water uptake behavior and their influence on morphology. To elucidate the significance of fulvic acids and the hygroscopic behavior observed so far for the real atmosphere, systematic investigations should be performed with authentic atmospheric HULIS from a range of locations.

In order to better understand the processing of soot particles in the atmosphere it would be necessary to further investigate combustion products, which includes the solid and gas phase, emitted by different combustion sources. We could show that emitted volatile organic compounds after oxidation and condensation on soot particles strongly influence their behavior. This influence is manifested by the change in water uptake ability of the soot, which is accompanied by the change in their cloud condensation nuclei ability and absorption/scattering properties, and by the change in trace gas uptake in the soot particles in presence of light. A systematic approach to measure the effects of these organic compounds would be necessary. Such investigations would include more systematic smog chamber studies, the characterization of the single soot particles depending on their processing, water uptake behavior studies combined with experiments on their scattering/absorption ability. But also studies on the interplay of these organic compounds with trace gases are necessary. Studies with proxy compounds like levoglucosan or tannic acid would further improve our knowledge on atmospheric effects of such emission products in the atmosphere.
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