Photochemical Aging Processes in Iron Containing Aerosols

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"Don’t be afraid to let the drama play out."

Ben Bernanke, Princeton University commencement speech, 2013
Abstract

Aerosol aging refers to the multitude of physical and chemical transformations that atmospheric particles undergo, which plays an important role in the impact on climate, air quality and public health. Out of many different aerosol types in the atmosphere, aqueous particles are of particular interest as photochemistry and radical reactions in the liquid phase are the main drivers of aerosol chemical conversions. Compared to the uptake of oxidants (e.g., •OH, O₃) from the gas phase, which are often reacting at or near the surface, photochemically active radiation penetrates the entire volume of aerosol particles, generating radicals throughout their bulk. In the lower troposphere, where UV light intensity with sufficiently low wavelength to directly photolyze aerosol components is low, indirect photochemistry (catalyzing redox processes of non-absorbing molecules) is especially relevant. Important indirect photochemical processes are initiated by either transition metal complexes or photosensitizers, both acting as photocatalysts for aerosol oxidation. We choose iron(III)-citrate (Fe³⁺(Cit)) induced citric acid (CA) degradation as a model system due to the abundance of carboxylate complexes and reactivity of Fe³⁺(Cit) in the atmosphere, and because CA is a good proxy for carboxylic acids in secondary organic aerosol (SOA) and the thermodynamic properties of CA have been studied in detail. Fe³⁺(Cit) absorption extends far into the blue spectral range, inducing the reduction of iron(III) to iron(II) and the oxidation of carboxylate ligands. In the presence of O₂, ensuing production of •OH and HO₂• will lead to more decarboxylation, production of oxygenated volatile organic compounds, as well as re-oxidation of iron(II) back to iron(III), closing this photocatalytic cycle, which is an important sink of organic acids in the troposphere.

It has recently been recognized that aqueous aerosol particles may attain highly viscous, semi-solid, or even glassy states under a wide range of atmospheric conditions. While the impact of reduced molecular mobility in highly viscous particles on dark chemistry has received substantial attention over the last decade, systematic studies on the effect of high viscosity on photochemical processes are scarce. In order to fill the gap, we developed a multilayered photochemical reaction and diffusivity (PRAD) model targeted at the Fe³⁺(Cit)/CA photochemistry system, to assess how viscosity and diffusivity influence photochemical processes. While Fe³⁺(Cit) photochemistry is reasonably well established, there are still a number of ill-constrained parameters in the model, such as the diffusivity of CO₂ and O₂ in the citric acid solution, the re-oxidation pathways and their reaction constants of iron(II) to iron(III). Therefore, we conducted experiments with single aqueous Fe³⁺(Cit)/CA particles levitated in electrodynamic balance to determine some of these
Pulsed light exposure experiments with particles in a N\textsubscript{2} atmosphere are used to derive the diffusivities of CO\textsubscript{2} and H\textsubscript{2}O at different relative humidities. Both agree with the Stokes-Einstein relationship for medium viscosities at intermediate RH (\(\sim 25 - 40\%\) RH), but are higher than these predictions under very dry high-viscosity conditions. We observe a cross-over of CO\textsubscript{2} and H\textsubscript{2}O diffusivities, resulting from different molecular interactions. Furthermore, O\textsubscript{2} re-oxidation measurements of iron(III) from photoreduced iron(II) help constrain the diffusivity of O\textsubscript{2} in aqueous citric acid droplet and the reaction rate of direct oxidation of Fe\textsuperscript{III}H(CCit) by O\textsubscript{2} utilizing the PRAD model. Long time irradiation experiments of Fe\textsuperscript{III}(Cit)/CA particles in O\textsubscript{2} show very significant mass loss (up to 80\%) due to the continuous degradation of citric acid in the photocatalytic cycle with loss of volatile species to the gas phase. Simulations with the PRAD model produce similar mass loss rates, indicating that our model captures the dominant chemistry and transport during irradiation. According to the concentration profile of each species calculated by the model, we conclude that the slower particle mass loss rate at lower RH is due to the condensed phase transport limitation of O\textsubscript{2} from the surface to the bulk of the particle. As iron in the atmospheric particles may be present as mineral dust inclusions, we studied aqueous citric acid particles containing Fe\textsubscript{3}O\textsubscript{3} nanoparticles (< 50 nm) and Arizona test dust particles (0–3 \(\mu\)m). These solid inclusions catalyze citric acid degradation as well, but the degradation is limited by the availability of dissolved iron. Finally, the PRAD model was used to predict photochemical degradation of aqueous citric acid droplets under atmospheric conditions. The model shows significant degradation of citric acid, and in highly viscous particles, the degradation process is limited by O\textsubscript{2} diffusivity, which is not only important for aerosol aging processes, but can also affect public health due to the longer preserved time of reactive oxygen species and free organic radicals.
Zusammenfassung

Der Einfluss atmosphärischer Aerosolteilchen auf Klima, Luftqualität und Gesundheit wird wesentlich durch die chemischen und physikalische Alterungsprozesse beeinflusst, die diese Teilchen erfahren. Unter den vielen Teilchentypen sind wässrige Teilchen von besonderem Interesse, da in ihnen photochemische und Radialreaktionen wichtig für ihre Alterung sind. Direkte Aufnahme von Oxidanzien wie \( \cdot \text{OH} \) oder \( \text{O}_3 \) aus der Gasphase ist oft durch die Oberflächenakkommodation limitiert, während photochemische Radikalproduktion im gesamten Volumen der Teilchen stattfindet. In der unteren Troposphäre ist die UV-Strahlung zu niedrig, um direkt photochemisch Radikale zu erzeugen. Hier sind indirekte photochemische Prozesse, die durch Metallkomplexe oder organische Photosensibilisatoren ausgelöst werden von besonderer Wichtigkeit für die Oxidation von Aerosolteilchen. In dieser Arbeit wurde durch der durch Eisenzitrat initierte photochemische Abbau von Zitronensäure als chemisches Modellsystem gewählt, zum einen weil sowohl Eisenzitrat als auch Zitronensäure in der Atmosphäre nachgewiesen sind, zum anderen weil die Thermodynamik der Zitronensäure gut untersucht ist. Eisenzitrat absorbiert sichtbare Strahlung bis weit in den blauen Spektralbereich, wobei angeregtes Fe(III) zu Fe(II) reduziert wird und eine Carboxylgruppe der Zitronensäure oxidiert wird. Im Beisein von Sauerstoff werden Peroxyradikale (wie \( \cdot \text{OH} \) und \( \text{HO}_2 \cdot \)) produziert, die zu weiterer Decarboxylierung und Produktion von volatilen organischen Molekülen führen, sowie das Fe(II) wieder zu Fe(III) oxidieren, womit der der photokatalytische Kreis geschlossen wird.

In den zurückliegenden Jahren hat sich die Erkenntnis verfestigt, dass organische Aerosolteilchen unter trockenen und/oder kalten atmosphärischen Bedingungen als sehr viskose Flüssigkeiten bis hin zu gläsernen, amorphen Festkörpern vorliegen können. Während einige Untersuchungen zum Verhalten solcher Teilchen bei Dunkelreaktionen bereits vorliegen, fehlen bislang Studien zum Einfluss solcher Phasenzustände auf die Photochemie dieser Teilchen. Um diese Lücke zu füllen, wurde in dieser Arbeit ein numerisches Modell (Photochemical Reaction and Diffusion, PRAD) für das Eisenzitrat/Zitronensäure-System entwickelt, um zu untersuchen, wie Viskosität und damit einhergehende Diffusionslimitierungen sich auf die Photochemie auswirken. Obwohl die Photochemie von Eisenzitrat relativ gut untersucht ist, fehlen doch genaue Kenntnisse über wichtige Parameter eines solchen Modells, wie z. B. die Diffusivität von CO\(_2\) und O\(_2\) in wässriger Zitronensäure, oder Reaktionskonstanten für die Oxidation von Fe(II) zu Fe(III). Deshalb wurden im Rahmen dieser Arbeit zielgerichtet Experimente an levitierten Einzelteilchen in einer elektrodynamischen Falle durchgeführt, um diese Parameter zu bestimmen, bzw. besser
abzuschätzen.

# Contents

**Abstract** iii  
**Zusammenfassung** v  
**Table of contents** viii  

## 1 Introduction 1  
1.1 Atmospheric aerosols ........................................... 1  
1.2 Aerosol aging ................................................... 3  
1.3 Photochemistry in iron containing aerosols ................. 4  
1.4 Kinetic transport limitations and chemical reactivity ....... 7  
1.5 Motivation and outline of the thesis ......................... 10  

## 2 Carbon dioxide diffusivity in single, levitated organic aerosol particles 13  
2.1 Introduction ..................................................... 13  
2.2 Experimental section ........................................... 15  
2.3 Results and discussion .......................................... 15  
2.4 Supporting Information ......................................... 24  
2.4.1 Rapid refractive index change ............................... 24  
2.4.2 Mass-loss retrieval considering density and refractive index change during loss of CO$_2$ ........................................... 26  
2.4.3 Raw data of the experiment under dry conditions ........ 27  
2.4.4 Experiment at 25% relative humidity ....................... 28  

## 3 Photochemical degradation of iron(III)-citrate/citric acid aerosol quantified with single, levitated particle experiments 29  
3.1 Introduction ..................................................... 30  
3.2 Experiment ....................................................... 32  
3.2.1 Sample preparation ........................................... 32  
3.2.2 Experimental setup .......................................... 33  
3.3 Photochemical reaction and diffusion (PRAD) model .......... 33  
3.4 Results and discussion .......................................... 38  
3.4.1 The determination of recovery rate by O$_2$ ................ 38  
3.4.2 The effect of RH on photocatalytic degradation ............ 42
4 Photocatalytic degradation of single, levitated organic aerosol particles containing iron nanoparticles or Arizona test dust

4.1 Introduction ................................................................. 48
4.2 Experiment ................................................................. 49
4.3 Photochemical reaction and diffusion (PRAD) model ................................ 50
4.4 Results and discussion ...................................................... 50
  4.4.1 Photochemical degradation in aqueous Fe$^{III}$(Cit)/CA droplets ........ 50
  4.4.2 The effect of available iron ........................................ 52
  4.4.3 Predication of photochemical aging in iron containing aerosols under atmospheric conditions ...................................................... 53
4.5 Summary and conclusions .................................................. 54

5 Summary and outlook .......................................................... 57
  5.1 Summary ..................................................................... 57
  5.2 Outlook ..................................................................... 59

A Parameters used in PRAD model ............................................... 63

List of figures ........................................................................ 67
List of tables .......................................................................... 69
References ............................................................................ 71
Acknowledgements ................................................................. 85
Chapter 1

Introduction

1.1 Atmospheric aerosols

Aerosol particles are liquid or solid particles suspended in the atmosphere. They can originate from either natural or anthropogenic sources, both of which can be further classified as either directly emitted as particles (primary aerosol) or formed by gas-particle conversion processes in the atmosphere (secondary aerosol). Sources of primary aerosol particles mainly involve wind-brown mineral dust, volcanic eruptions, sea spray, biomass burning, biological materials, fossil fuel combustion and industrial processes. Secondary aerosol particles are generated by the nucleation of new particles, condensation, and heterogeneous and multiphase chemical reactions in existing particles (Hallquist et al., 2009). Different types of aerosol particles are ubiquitously distributed throughout the entire atmosphere, ranging in size from nanometers up to tens or hundreds of micrometers. They can be divided roughly into three size modes: nuclei mode (< 0.1 μm in diameter), accumulation mode (0.1–2.5 μm in diameter) and coarse mode (> 2.5 μm in diameter). Particles in the nuclei mode are generally fresh particles from the nucleation of atmospheric gas phase species. They tend to grow via coagulation and condensation of vapors into the accumulation mode. Coarse particles are usually produced by mechanical processes and can settle out of the atmosphere in a short time because of sufficiently high sedimentation velocities. In contrast to particles in nuclei and coarse modes, particles in the accumulation mode have less efficient removal mechanisms, resulting in a considerably longer atmospheric lifetime (days to weeks), and thus being able to be transported over long distances (Seinfeld and Pandis, 2006).

The composition of aerosol particles is extremely diverse, depending on location and time. The variability of both mass concentration and composition of atmospheric aerosol is shown in Figure 1.1. Based on measurements with aerosol mass spectrometers (AMS) at various sampling locations, the major components in the particulate phase (< 1 μm in diameter, PM$_1$) are organics (green), sulfate (red), nitrate (blue), ammonium (orange), and chloride (purple) (Zhang et al., 2007). Organic compounds make up a major fraction (18–70%) in the study of Zhang et al. (2007), and the fraction can even rise up to 90% in tropical forested areas (Kanakidou et al., 2005). Due to various emission sources and
complex physical and chemical processes involved, the organic fraction comprises myriads of different chemical compounds. For example, Hamilton et al. (2004) isolated more than 10,000 individual organic species ranging in functionality from alkanes to polyoxygenated species. Therefore, it is common to use bulk properties to identify organic species, such as volatility, oxygen to carbon (O:C) ratio, or solubility in water. Water soluble organic carbon (WSOC) can account for 5–85% of total carbon (TC) mass, and 10–95% of organic carbon (OC) mass in different types of aerosol samples (Mader et al., 2004), and usually contain (di-/poly-)carboxylic acids, polyols, polyphenols, sugars and other oxygenated multifunctional compounds (Decesari et al., 2000; Rogge et al., 1993; Saxena and Hildemann, 1996). WSOC can mix with other components in aerosol particles and plays a crucial role in atmospheric processes.

Aerosol particles have been demonstrated to have a great impact on climate, air quality, and human health. As reported by Intergovernmental Panel on Climate Change (IPCC), aerosols affect climate in direct, semi-direct, and indirect ways (Boucher et al., 2013): The direct effect is caused by aerosol-radiation interactions (ari) which can both cool (by scattering) and warm (by absorption) the climate system. If more absorbing aerosol particles (e.g., black carbon) are involved, heating of aerosols by solar absorption can decrease relative humidity and then burn off clouds. This is called a semi-direct effect. Even though the uncertainties of absorbing aerosols remain large, most studies agree that the overall radiative effect from anthropogenic aerosols is to cool the planet. There are two indi-
1.2 Aerosol aging

Aerosol aging refers to multiple physical and chemical transformations of atmospheric particles during their days to weeks lifetime. Physical transformations mainly include coagulation of several particles (Ramabhadran et al., 1976), gas-particle partitioning (Donahue et al., 2006, 2009), and phase transitions within particles (Freedman, 2017; Marcolli and Krieger, 2006). Chemical transformations are way more complicated. They can be driven by condensed phase reactions, heterogeneous uptake of oxidants (e.g., \( \cdot \)OH, O\(_3\), NO\(_2\) and NO\(_3\)), and gas phase reactions followed by the condensation of low-volatility products (Rudich et al., 2007). Photochemistry induced aerosol aging is also an important process, which will be discussed in Section 1.3 and will be the focus of this thesis. As Jimenez et al. (2009) reported, there are three pathways involved in the chemical aging of organic aerosol particles: fragmentation, oligomerization and functionalization, as shown in Figure 1.2c. Oligomerization and functionalization decrease the volatility mainly due to the increase of molecular mass and O:C ratio, respectively, while fragmentation can produce
more volatile compounds (e.g., CO$_2$) mainly due to the decrease of molecular weight. The oxidation of organic aerosols (e.g., induced by $^\cdot$OH or O$_3$) usually produces less volatile, more hygroscopic species with higher O:C ratio, as shown in Figure 1.2a and 1.2b.

Aerosol aging can change important properties of particles, such as optical properties, hygrosopicity and toxicity, all of which will in turn influence the environment and public health. Chemical processing can increase the absorption of aerosol particles (‘browning’) due to the production of highly conjugated molecules (Bones et al., 2010; Laskin et al., 2010; Nozière, 2005; Updyke et al., 2012). Hygrosopicity of aerosol particles governs the uptake or loss of water, thus influencing their optical properties, their effectiveness as cloud condensation nuclei, and their respiratory track deposition due to size change. Since there is a competition between the formation of more highly oxidized polar compounds (more hygroscopic), and the formation of longer-chained oligomers (less hygroscopic), hygrosopicity can either increase or decrease during the aging of organic aerosols (Varutbangkul et al., 2006; Vesna et al., 2008). Because aerosol aging alters the chemical composition of particles, their threat to public health may increase due to more toxic species generation. For instance, protein nitration can increase the allergenic potential (Franze et al., 2005), and ozonolysis of cypermethrin can form toxic and more polar compounds (Segal-Rosenheimer and Dubowski, 2007).

1.3 Photochemistry in iron containing aerosols

The Earth atmosphere is predominantly made up of molecular nitrogen (∼78%) and molecular oxygen (∼21%), both of which are highly stable molecules, at least in the troposphere. Consequently, photochemistry in the atmosphere (either in the gas phase or in the particle phase) is quite important to initiate aerosol aging. Photochemically produced free radicals in the gas phase (mainly $^\cdot$OH) can be taken up by aerosol particles, inducing heterogeneous chemistry. However, the uptake is generally limited by the collision rate and possibly condensed phase diffusivity, restricting chemical reaction to the surface region of the particle. In contrast, light can penetrate the whole volume of the particle, generating radicals throughout the particle. If the energy of light is high enough (usually refers to the UV part of the solar spectrum), it can cause bond cleavage or rearrangement directly in a molecule; this is referred to as direct photochemistry. By contrast, in the lower troposphere where UV light intensity is low, indirect photochemistry initiated by visible radiation is significant. Important indirect photochemical processes are transition metal complex photochemistry and photosensitized processes, which can induce electron-transfer or energy-transfer reactions (Corral Arroyo et al., 2018; George et al., 2015). This work will focus on iron carboxylate catalyzed photochemistry due to its abundance and reactivity in the atmosphere.

Iron is the most abundant transition metal in the earth’s crust. Wind can pick up mineral dust particles and transport them over long distances. Wind erosion is the main source of iron in the atmosphere, as well as anthopogenic activities such as industrial processes and combustion (Deguillaume et al., 2005). Iron reaches the atmosphere either
Figure 1.2: (a) Organic aerosol aging with α-pinene as an example. The x axis is volatility. The left y axis is oxidation state, estimated by O:C ratio. The right y axis shows the approximate hygroscopicity. All the first generation from the α-pinene + O$_3$ reaction are distributed according to the blue contours, with mean properties indicated by the blue star. Lower-volatility products are less volatile and more oxidized, shown by green areas to the upper left of blue contours. Products from functionalizations by adding =O and –OH are roughly within the limits indicated by the red dashed lines. The modeled condensed-phase products after 1.5 lifetimes of •OH oxidation are shown with purple contours and the yellow star. (b) Evolution of condensed-phase O:C ratio versus approximate •OH exposure during simulated aging. The blue and yellow stars are the same as shown in (a). (c) Reactions can be classified into three categories: fragmentation, functionalization and oligomerization, dependent on whether the carbon number decreases, stays the same, or increases. The branching ratio (β) between these pathways is crucial. Functionalization will reduce volatility significantly, whereas fragmentation can produce more volatile species. Reproduced from Jimenez et al. (2009).
as ‘structural iron’ trapped in the crystal lattice of aluminosilicate minerals, or as ‘free iron’ in the form of oxides (e.g., hematite (Fe$_2$O$_3$) and goethite (α-FeOOH) from desert soils) (Lafon et al., 2004), or sulfides (e.g., FeS$_2$, FeS and Fe$_{1-x}$S from coal combustion) (Kopcewicz and Kopcewicz, 2001). Once iron containing particles reach the atmosphere, they begin to participate in various chemical processes. Depending on parameters such as temperature, pH value, ionic strength and concentration of involved substances, iron can combine with inorganic or organic ligands to form complexes (Deguillaume et al., 2005; Faust and Hoigné, 1990; Kieber et al., 2005). In the absence of soluble organic compounds, iron is mainly found as low molecular weight species complexed with the hydroxide anion (OH$^-$), sulfate (SO$_4^{2-}$) and sulfite (SO$_3^{2-}$) (Brandt and van Eldik, 1995; Hofmann et al., 1991; Weschler et al., 1986). As a major component in atmospheric aerosol particles (discussed in Section 1.1), organic compounds have received more and more attention as potential ligands for iron(III) complexation. For instance, as a fraction of WSOC, Humic Like Substances (HULIS) have been reported to be strong chelating ligands with iron(III), even though the composition of HULIS is not fully understood (Dou et al., 2015; Kieber et al., 2003; Okochi and Brimblecombe, 2002; Willey et al., 2000). Oxalate and other carboxylate have been identified to be important ligands for iron(III) because they are available in sufficient amount (Chebbi and Carlier, 1996; Kahnt et al., 2014; Kawamura et al., 1985), and the carboxylate groups are acidic enough to dissociate to chelate with iron(III) at atmospheric pH values (Okochi and Brimblecombe, 2002).

In atmospheric aqueous phases, iron normally exists in oxidation states (II) and (III), and they can convert into each other via a so called redox cycling. The ratio between iron(II) and iron(III) in aerosol particles is quite variable, which depends on several factors such as the presence of light, the presence of oxidizing compounds and the presence of ligands. For example, iron(III) carboxylate complexes [Fe$^{III}$(OOC–R)]$^{2+}$ are well-known photoactive compounds (Wang et al., 2012; Weller et al., 2013, 2014). They can easily get excited by light in the UV-VIS range, inducing ligand-to-metal charge transfer (LMCT) (Cieślak et al., 2004), which is an inner sphere electron transfer (i.e., the electron transfer occurs via a covalently bound bridging ligand) from the carboxylate group to the iron. Investigations using time resolved transient spectroscopy reported the formation of long lived radical complexes, [Fe$^{II}$(*OOC–R)]$^{2+}$, with lifetimes of the order of a millisecond, followed by the dissociation to the organic radical R–COO$^•$ and an Fe$^{II}$ aquacomplex (Feng et al., 2007; Glebov et al., 2011; Pozdnyakov et al., 2009; Zhang et al., 2009):

\[
[\text{Fe}^{\text{III}}(\text{OOC–R})^{2+} + h\nu \rightarrow [\text{Fe}^{\text{III}}(\text{OOC–R})]^{2+*} \quad (R1.1)
\]

\[
[\text{Fe}^{\text{III}}(\text{OOC–R})]^{2+*} \rightarrow [\text{Fe}^{\text{II}}(*\text{OOC–R})]^{2+} \quad (R1.2)
\]

\[
[\text{Fe}^{\text{II}}(*\text{OOC–R})]^{2+} \rightarrow \text{Fe}^{2+} + \text{R–COO}^• \quad (R1.3)
\]

R–COO$^•$ will decarboxylate almost instantaneously ($k_{R1.4} \approx 10^9 - 10^{12}$ s$^{-1}$) (Abel et al.,...
1.4 Kinetic transport limitations and chemical reactivity

Aerosol particles in the atmosphere can be liquid or solid or a mixture of both, depending on their composition and ambient conditions (Marcolli et al., 2004, Martin, 2000). Marcolli et al. (2004) found that organic-rich particles tend to become amorphous solid instead of crystallizing as temperature is decreasing. Therefore, organic aerosol particles mostly exist in a highly viscous or even glassy, amorphous solid state under dry and/or cold conditions, limiting the diffusivity of their components such as water, oxidants and organic molecules (Koop et al., 2011, Shiraiwa et al., 2011, 2017, Virtanen et al., 2010, Zobrist et al., 2008, 2011). The inverse relationship between diffusivity $D$ and viscosity $\eta$ can be described by the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi \eta r},$$

(1.1)

where $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$), $T$ is the temperature, and $r$ is the dynamic radius of the diffusing molecule. Assuming a molecular radius of 1 nm, the calculated $D$ with different $\eta$ at room temperature is plotted (Figure 1.4, reproduced from


$$R−\text{COO}^• \rightarrow R^• + \text{CO}_2 \quad \text{(R1.4)}$$

The alkyl radical $R^•$ will react rapidly with dissolved $\text{O}_2$ ($\sim 3 \times 10^{-4}$ M at atmospheric pressure), producing a peroxo radical with $k_{R1.5} \approx 2 \times 10^9$ s$^{-1}$ (von Sonntag and Schuchmann 1991):

$$R^• + \text{O}_2 \rightarrow \text{RO}_2^• \quad \text{(R1.5)}$$

Subsequent reactions of $R^•$ and $\text{RO}_2^•$ can be specific depending on the type of ligand and its substitution. In this work we investigate iron(III)-citrate ($\text{[Fe}^{\text{III}}(\text{OOCCH}_2\text{C(OH)})_\text{3C(OH)}]$), short Fe$^{\text{III}}$(Cit)), as a model species. Fe$^{\text{III}}$(Cit) photochemistry is well established in both solution (Abida et al., 2012, Faust and Zepp, 1993, Pozdnyakov et al., 2012) and solid states (Abrahamson et al., 1994). As schematically described in Figure 1.3, Fe$^{\text{III}}$(Cit) absorbs light up to around 500 nm, inducing LMCT, followed by immediate decarboxylation of the central carboxyl group, since the hydroxyl group adjacent to a carboxyl group facilitates decarboxylation (Weller et al., 2013). In the presence of $\text{O}_2$, oxidants such as $\text{HO}_2^•$ and $\text{H}_2\text{O}_2$ will be produced, which can oxidize Fe$^{\text{II}}$ back to Fe$^{\text{III}}$ via Fenton reactions (Fenton, 1894), with additional production of oxidants. Fe$^{\text{III}}$ then combines with another citric acid in this aqueous system, closing the photocatalytic cycle, in which iron acts as a catalyst. In addition, the generation of ROS and peroxo radicals in the atmospheric aerosol phase can lead to further decarboxylation and more production of oxygenated volatile organic compounds (OVOC) (e.g., acetone) (Pozdnyakov et al., 2008, Wang et al., 2012). Therefore, this photodegradation process is potentially an important sink of carboxylate groups in the troposphere.
Figure 1.3: Photocatalytic cycle of Fe\textsuperscript{III}-citrate complex in an aqueous particle containing citric acid.

Koop et al. (2011), which varies more than 15 orders of magnitude from $\sim 10^{-5}$ cm\textsuperscript{2} s\textsuperscript{-1} in liquid water to $\sim 10^{-20}$ cm\textsuperscript{2} s\textsuperscript{-1} in a solid glass due to the large range of viscosity. Also shown in Figure 1.4 are images of familiar substances and their approximate viscosities. Based on viscosity values, Shiraiwa et al. (2011) classified substances into liquids ($< 10^2$ Pa s), semi-solids ($\sim 10^2 - 10^{12}$ Pa s) and solids ($> 10^{12}$ Pa s), and inferred the e-folding times of equilibration for various particle diameters, which are shown in the bottom panel of Figure 1.4. However, even though the Stokes–Einstein relationship works well over a large range of viscosities for the prediction of diffusion coefficients, it can break down in highly viscous systems, especially for small molecules such as water (Bastelberger et al., 2017; Champion et al., 2000; Power et al., 2013). It is therefore necessary to measure diffusion coefficients for various compounds independently, which is one part of this thesis: measuring diffusivities of H$_2$O and CO$_2$ in Fe\textsuperscript{III}-citrate/citric acid aqueous particles for viscous cases (see Chapter 2).

The reduced mobility of aerosol constituents in highly viscous particles can affect particle reactivity through several ways such as limiting the reactive uptake, and slowing diffusion of chemical species from the surface into the bulk, thus potentially limiting those to surface reactions (Berkemeier et al., 2016; Steimer et al., 2015a; Vlasenko et al., 2009). There are two types of mechanisms to describe surface reaction kinetics: the Eley-Rideal mechanism (ER), which refers to gaseous molecules reacting directly with molecules present on the surface upon collision; the Langmuir-Hinshelwood mechanism (LH), which refers to gaseous molecules adsorbed at available surface sites prior to the reaction. Most of atmospheric surface reactions can be described with the LH mechanism. The interactions of gas phase reactants with the particle phase reactants involves both surface reactions and bulk reactions. According to Ammann et al. (2013) and Berkemeier et al. (2013), there are
two cases when it comes to reactions within the particle bulk. In the first case, the gas-phase reactant $X$ diffuses throughout the condensed phase quickly enough to compensate its chemical loss due to the reaction with bulk phase reactant $Y$. Then the loss rate of $Y$ is treated as a common second-order reaction in a homogeneously mixed condensed phase:

\[
\frac{d[Y]_b}{dt} = -k_{II}^b [X]_b [Y]_b = -k_{II}^b [X]_b [Y]_b = -k_{II}^b H_X p_X [Y]_b,
\]

(1.2)

where $[X]_b$ and $[Y]_b$ are the concentrations of $X$ and $Y$ in the particle bulk, $k_{II}^b$ is the second-order rate coefficient, $H_X$ is the Henry’s law constant of $X$, and $p_X$ is the pressure of $X$ in the system. In this case, the overall reaction rate is limited by the volume of the system. The other case applies when $X$ diffuses slowly in comparison to the reaction rate with $Y$, which is called reacto-diffusion limited kinetic regime. There is a concentration gradient of $X$ forming in the particle bulk from surface towards the center. And the overall reaction rate is limited by the diffusion coefficient of $X$ in the condensed phase, $D_X$. The
reacto-diffusive length $l$:

$$l = \sqrt{\frac{D_X}{k^H_b[Y]_b}},$$  

(1.3)

is defined to characterize the distance $X$ can diffuse into the condensed phase before it reacts (Hanson et al., 1994). If $l$ is larger than the particle dimension, we can treat the system as the first case (i.e., Eq. 1.2). If not, then the loss rate of $Y$ can be described as (Hanson et al., 1994):

$$\frac{d[Y]_b}{dt} = -H_X RT \sqrt{D_X k^H_b[Y]_b} \left[ \coth \left( \frac{r}{l} \right) - \left( \frac{l}{r} \right) \right] \frac{S_p}{V_p} [X]_g,$$

(1.4)

where $R$ is the gas constant, $T$ is the temperature, $r$ is the radius of the particle, $S_p$ is the surface area of the particle, $V_p$ is the volume of the particle, and $[X]_g$ is the concentration of $X$ in the gas phase. Note that in Eq. 1.4, even though diffusivity is considered as a factor, only the condensed phase diffusivity of gaseous molecule $X$ is taken into account, with $Y$ considered to stay well-mixed. The reacto-diffusive limitations have been demonstrated to be widely existing in reactive uptake induced aerosol aging processes. For instance, Steimer et al. (2015a) observed that when relative humidity is lower than 92%, the ozonolysis of shikimic acid is no longer reaction limited, instead it is limited by the diffusivity of O$_3$, showing a pronounced concentration gradient of O$_3$. In addition, this measurement has already been successfully simulated by a kinetic multilayer model of aerosol surface and bulk chemistry, providing a depth-resolved profile of O$_3$ in the aerosol particle (Berkemeier et al., 2016), which can not be described with classical resistor models.

The viscosity not only affects the dark chemical reactions, but also can directly change the photochemical reaction rate. For instance, Lignell et al. (2014) found that the photolysis rate of 2,4-dinitrophenol dissolved in 1-octanol or secondary organic material (SOM) increases by more than one order of magnitude than that dissolved in an aqueous solution, since C-H bonds are better hydrogen-atom donors than O-H bonds. And they proposed that the increasing viscosity of the SOM matrix constrains the molecular motion, thus suppressing the hydrogen atom transfer reaction to the photoexcited 2,4-dinitrophenol. Similarly, the increase of viscosity causes a slow electron transfer from the photoexcited triplet state of zinc cytochrome c (Ivković-Jensen and Kostić, 1997). This thesis will provide more data on the interactions between transport limitations and photochemical processes using Fe$^{III}$(Cit) photolysis system (see Chapter 3).

1.5 Motivation and outline of the thesis

As discussed in detail in the previous sections, aerosol aging plays a significant role in the impact of aerosols on climate, air quality and human health. Out of many different aerosol types in the atmosphere, aqueous organic particles are the dominant form, in which photochemistry and radical reactions are the main drivers of aerosol chemical conversions. Compared to the uptake of oxidants (e.g., *OH or O$_3$) from the gas phase, which can be surface accommodation limited, photochemically active radiation penetrate the whole
volume of aerosol particles, generating radicals throughout their bulk. In the lower troposphere, where UV light intensity with sufficiently low wavelength to directly photolyze aerosol components is low, indirect photochemistry (catalyzing redox processes of non-absorbing molecules) is especially relevant. Important indirect photochemical processes are initiated by either transition metal complexes or photosensitizers, both acting as photocatalysts for aerosol oxidation. We are interested in Fe$^{III}$(Cit) catalyzed photochemistry due to its abundance and reactivity in the atmosphere. This complex can get excited by light up to 500 nm, inducing the reduction of Fe$^{III}$ to Fe$^{II}$ and the oxidation of carboxylate ligands. In the presence of O$_2$, ensuing production of •OH and HO$_2$• will lead to more decarboxylation and oxygenated volatile organic compounds (OVOC) production, as well as re-oxidize Fe$^{II}$ back to Fe$^{III}$, closing this photocatalytic cycle, which is an important sink of organic acid in the troposphere.

It has been recently recognized that aqueous aerosol particles may attain highly viscous, semi-solid or even glassy states under a wide range of conditions in the atmosphere. The reduced mobility of aerosol constituents in highly viscous particles can have a profound impact on particle reactivity. However, while the impact on dark chemical reactions has received substantial attention, systematic studies on the effect of high viscosity on photochemical processes are scarce. The reduced mobility and low water content can influence the indirect photochemical processes via affecting the initial absorption process, charge and energy transfer, and preventing the diffusion of intermediates. In turn, the ensuing oxidation processes can also affect the microphysical properties such as viscosity through building up various products with different molecular weights and different oxidation states. Therefore, there are feedbacks existing that link microphysics and photochemistry in aerosol particles.

The work presented in this thesis is part of a joint project with colleagues at Paul Scherrer Institute (PSI). The aim of this large project is to establish a comprehensive understanding on how and to what extent indirect photochemical aerosol aging processes are affected by transport limitations in viscous aqueous particles. For the assessment of the model system: Fe$^{III}$(Cit) induced citric acid degradation, a wide range of techniques have been used by the ETH and the PSI group. Mass and size changes of single levitated particles, and diffusivities of CO$_2$ and H$_2$O in these particles have been measured in an electrodynamic balance (EDB) at ETH. Spatially resolved O:C ratios, carbon functional groups, and iron oxidation states have been measured by in situ scanning transmission X-ray microscopy (STXM) at PSI. Measurements of OVOC formation rates and quantification of radical budgets have been performed in an irradiated coated wall flow tube (CWFT) together with offline analysis of non-volatile organic compounds by High performance liquid chromatography-mass spectrometry (HPLC-MS) at PSI. In each of these analysis, the model system is followed over time as a function of irradiation, relative humidity and temperature. In parallel, a multilayer kinetic model including chemical reactions and transport of major species has been developed to assist the integration of the results. With well-defined and physically constrained parameters, we can predict the evolution of products as well as organic acid degradation in the particle phase under atmospheric
This thesis focuses on the mass, size and diffusivity measurements of single aqueous particles (radius \(\sim 10 \mu m\)) levitated in EDB as well as the development of a numerical model. Different irradiation intensities and periods, different temperatures and relative humidities are applied to investigate the interactions between aerosol reactivity and transport limitations in the condensed phase. Meanwhile, the numerical model is used to simulate the experimental results, getting a in-depth gradient profile of each species inside the particle. Comparing model output with experimental data enables us to determine or at least constrain some of the crucial parameters, such as equilibrium constants, chemical reaction rates and liquid phase diffusion coefficients. Finally, these lab and model results will be integrated with outcomes from PSI, providing a substantial support for the prediction of aerosol aging in the atmosphere.

Chapter 2. Carbon dioxide diffusivity in single, levitated organic aerosol particles uses Fe\(^{III}\)(Cit) photochemically generated CO\(_2\) to deduce CO\(_2\) diffusivity in the aqueous citric acid particle at different viscosities. Together with water diffusivity deduced from the same system, they are compared with the Stokes-Einstein relationship based on viscosity measurements by other research groups. These data will help constrain kinetic limitations for condensed phase chemistry in secondary organic aerosol particles.

Chapter 3. Photochemical degradation of iron(III)-citrate/citric acid aerosol quantified with single, levitated particle experiments compares the measurements of Fe\(^{III}\) recovery efficiency either by O\(_2\) directly or by radicals at different relative humidities. The photochemical reaction and diffusion (PRAD) model is described in detail, which helps to deduce the diffusivity of O\(_2\) and to evaluate the two recovery pathways. Moreover, with the gradient profile inside the particle shown by the model, we can get a better understanding on how transport limitations influence the reaction kinetics.

Chapter 4. Photocatalytic degradation of single, levitated organic aerosol particles containing iron nanoparticles or Arizona test dust confirms the photocatalytic role of iron species dissolved in citric acid aqueous particles. The PRAD model is also applied to predict the photochemical degradation of carboxylate complexes in iron containing aerosols under atmospheric conditions.

Chapter 5. Summary and outlook summarizes the main findings of the PhD work along with suggestions for future research that are motivated from findings presented in this thesis.
Chapter 2

Carbon dioxide diffusivity in single, levitated organic aerosol particles


Abstract

The diffusivity of molecules relevant to condensed-phase chemistry within viscous secondary organic aerosol (SOA) remains highly uncertain. Whereas there has been an effort to characterize water diffusivity as well as the diffusivity of larger compounds, data are lacking almost entirely for small molecules, such as carbon dioxide (CO$_2$). Here we use photochemically generated CO$_2$ in single particles of aqueous citric acid as a SOA proxy, levitated in an electrodynamic balance, to deduce CO$_2$ diffusivity in the particle with unprecedented accuracy. For medium viscosities at intermediate relative humidities ($\sim 25 - 40\%$ RH), we find CO$_2$ diffusivities $D_{\text{CO}_2} \approx 10^{-14}$ m$^2$ s$^{-1}$, agreeing with the Stokes-Einstein relationship based on current viscosity data but 10 times lower than that for water. Conversely, under dry high-viscosity conditions, we find that $D_{\text{CO}_2} \approx 10^{-16}$ m$^2$ s$^{-1}$, which is 10 times higher than for water. We infer that the chemical degradation of atmospheric SOA particles will likely not be limited by CO$_2$ diffusivity.

2.1 Introduction

Organic aerosol particles make up 20–90% of the mass of sub-micron-size atmospheric particles depending on the location and time. These particles have significant impacts on climate as well as on human health, but their atmospheric processing is still not fully understood (Jimenez et al. 2009). Traditionally, these particles have been considered to be internally well-mixed liquids, but it became evident during the past decade that this does not hold true under dry and/or cold conditions, where they turn from the liquid state to a highly viscous or even glassy, amorphous solid state (Koop et al., 2011) Shiraiwa et al. 13
To predict atmospheric chemical processing and partitioning between gas and particle phase under these conditions, information on the rate of diffusion of oxidants, water, and volatile and nonvolatile compounds within these particles is needed. In particular, because CO$_2$ is the final product of organic aerosol oxidation, its diffusivity is important for estimating particle degradation, but no diffusivity data in viscous particles have been reported. In contrast, water diffusivity in organic aerosol has been measured in a number of studies in recent years using different techniques (Bones et al., 2012; Davies and Wilson, 2016; Lienhard et al., 2015; Price et al., 2014; Steimer et al., 2015b; Zobrist et al., 2011). These measurements, together with viscosity data proved that there are strong deviations from the Stokes-Einstein (S-E) relationship when applied to highly viscous organics (Power et al., 2013).

There are less data available for the diffusivity of molecules important for predicting reactivity and photochemistry (Davies and Wilson, 2015; Gržinić et al., 2015; Shiraiwa et al., 2011; Steimer et al., 2015b; Zhang et al., 2018) and for estimating the fate of toxic compounds during long-range transport (Abramson et al., 2013; Bastelberger et al., 2017; Shrivastava et al., 2017). Limited data are available for high-molecular-mass compounds for which the S-E relationship may provide a good approximation to estimate diffusivity (Chenyakin et al., 2017; Liu et al., 2016; Price et al., 2016; Ullmann et al., 2019; Ye et al., 2016). In addition, understanding atmospheric aging and repartitioning of molecules to the gas phase due to photochemistry will require diffusivity data of typical oxidants, such as O$_2$, **OH and HO$_2$**.

Here we will present a new method to measure CO$_2$ and H$_2$O diffusivity in organic aerosol simultaneously and with high accuracy by pulsed-light exposure experiments with a single, levitated aerosol particle. We used iron(III)-citrate (Fe$^{III}$(Cit)) photochemistry as a proxy for one of the main reactive mechanisms responsible for the chemical removal of carboxylic acids in the atmosphere (Weller et al., 2013, 2014). Light absorption by Fe$^{III}$(Cit) can occur up to 500 nm and induce ligand-to-metal charge transfer (reaction R1), followed by the immediate decarboxylation of the central carboxyl group (reaction R2), since the hydroxyl group adjacent to a carboxyl group facilitates decarboxylation (Pozdnyakov et al., 2012; Quici et al., 2007; Seraghni et al., 2012; Weller et al., 2013):

$$\text{Fe}^{III} (\text{Cit}) + h\nu \longrightarrow \text{Fe}^{II} + ^*\text{Cit}, \quad (R1)$$

$$^*\text{Cit} \longrightarrow \text{HO}^-\cdot\text{CR}_2 + \text{CO}_2 \uparrow. \quad (R2)$$

In the atmosphere with O$_2$ present, ensuing radical chemistry will lead to more decarboxylation and the productions of peroxides and oxygenated volatile organic compounds, contributing to further particle mass loss. The peroxides, in turn, allow the re-oxidation of Fe$^{II}$ to Fe$^{III}$, closing this photocatalytic cycle. Here, we constrain the chemistry to R1 and R2 by levitating the aqueous Fe$^{III}$(Cit) droplet in humidified nitrogen. CO$_2$ will diffuse out of the particle phase, which will decrease the particle mass and size. Water content (uptake or loss) will adjust due to this change in composition toward maintaining
the equilibrium with the relative humidity (RH) of the surrounding air. In this anaerobic system, the photochemistry will stop as soon as all Fe$^{III}$ has been reduced to Fe$^{II}$. We will show that the loss of CO$_2$ to the gas phase together with a readjustment of water can be measured accurately, and the diffusivity for both species can be determined with unprecedented accuracy.

2.2 Experimental section

The experimental setup used in our experiments has been described previously in-depth (Steimer et al., 2015b). In brief, an electrically charged aqueous particle is injected into an electrodynamic balance (EDB) by a droplet-on-demand generator (Hewlett-Packard 51633A ink jet cartridge, filled with a diluted aqueous solution). This EDB is of the double design (Davis et al., 1990), with a high AC voltage applied to two electrode rings and a DC voltage across hyperbolic end-caps generating an electric field to trap the particle. The DC field compensates the gravitational force of the particle and is adjusted automatically by a feedback loop to track the mass changes of the particle. The chamber that hosts the balance has three glass walls with an insulation vacuum between the two outer ones and a cooling liquid (ethanol) pumped through the two inner ones to control the temperature in the trap. RH in the chamber is regulated by adjusting the mixing ratio of a dry and humidified gas flow. The refractive index and size of spherical particles are measured by two Mie resonance spectroscopy-based methods: (i) A narrow-bandwidth tunable diode laser (TDL) with a scanning range of 765–781 nm is used to illuminate the particle at a scattering angle of $90^\circ$. At this angle, both transverse electric (TE) mode resonances and transverse magnetic (TM) mode resonances are measured one after the other to determine the refractive index and radius simultaneously with an accuracy of 0.005 in the refractive index and a corresponding accuracy of 2 nm in size (Steimer et al., 2015b). (ii) Simultaneously, the backscatter signal from a broad-band LED centered around 640 nm is recorded using a spectrograph with a slow-scan back-illuminated CCD (charge-coupled device) array detector to follow the radius change of the particle (Zardini et al., 2006). In the experiments described in this work, we use a typical total gas flow of 40 sccm (humidified nitrogen gas) and control the total pressure inside the cell at 600 torr. The typical initial radius of the particle is about $\sim 10 \mu$m. All experiments are done at 293 K, with different RHs (0, 25 and 37%). A frequency-doubled diode laser at a wavelength of 473 nm (gem 473, Laser Quantum) is used to induce photochemical processing.

2.3 Results and discussion

Figure 2.1a shows the temporal evolution of one Mie resonance wavelength in a typical irradiation experiment. The particle was kept in a humidified nitrogen atmosphere with constant RH and temperature until equilibrated. It was irradiated five times consecutively (irradiations #1 and #2 for 2 s each, irradiations #3 to #5 for 10 s each). Clearly, the resonance wavelength shifts toward a lower wavelength (blue shift) with each irradiation,
Figure 2.1: (a) Temporal evolution of Mie resonance wavelength for pulsed-light exposure experiments (37% RH at 293 K, initial particle size: 8.66 µm). Orange lines represent five periods of irradiations with durations of 2 s at 470±740 W cm\(^{-2}\) for #1 and #2, and 10 s at 470±740 W cm\(^{-2}\) for #3, #4, and #5. Horizontal lines indicate the equilibrated wavelength after irradiation #1, #2 and #3. (b) Zoomed-in view of irradiation #1.

but with decreasing amplitude until the shift becomes buried in the measurement noise for irradiations #4 and #5. An expanded scale of irradiation #1 is shown in Figure 2.1b. We identify three time scales: (i) a very rapid blue shift (\(\Delta \lambda \approx -0.98 \text{ nm}\)), which appears almost instantaneously (\(\tau_i \approx 2 \text{ s}\)), (ii) a slower (\(\tau_{ii} \approx 290 \text{ s}, \Delta \lambda \approx +0.20 \text{ nm}\)) red shift, followed by (iii) an even slower blue shift with \(\tau_{iii} \approx 3390 \text{ s}\) and \(\Delta \lambda \approx -0.40 \text{ nm}\). Shift (i) is caused by a refractive index change due to the rapid photochemically produced CO\(_2\) (reactions [R1] and [R2]). The second shift (ii) is interpreted to be a size (and mass) gain caused by water uptake due to water activity reductions induced by the photochemistry within the particle, and the third shift (iii) is interpreted to be a size decrease due to the slow loss of the CO\(_2\) to the gas phase. These will be discussed in more detail below. Clearly, our measurements indicate that the particle no longer photochemically reacts after irradiation #3 due to the complete transition of Fe\(^{III}\) to Fe\(^{II}\).

The resonance wavelength, \(\lambda(t)\), is ([Ray et al., 1991])

\[
\frac{\lambda(t)}{\lambda_0} = \frac{r(t)}{r_0} \frac{1}{1 - K \frac{n(t) - n_0}{n_0}},
\]

(2.1)

where \(\lambda_0\), \(r_0\), and \(n_0\) are the initial wavelength, radius, and refractive index, and \(r(t)\) and \(n(t)\) are the radius and refractive index at a later time, \(t\). \(K\) is a proportionality factor taken as constant 0.95 here ([Ray et al., 1991]). During the first 2 s of irradiation, we assume that any size change is negligible and the change in \(\lambda\) is entirely due to a change in refractive index. If the blue shift was caused by a loss of condensed-phase molecules to the gas phase, then it would be inevitably slower due to diffusional transport limitations.

Hence, Eq. [2.1] can be simplified to

\[
\Delta n = \frac{n_0}{K} \frac{\Delta \lambda}{\Delta \lambda + \lambda_0},
\]

(2.2)
2.3. Results and discussion

where $\Delta \lambda$ is the observed shift in wavelength and $\Delta n$ is the corresponding change in refractive index. With $n_0 = 1.483$ for the refractive index of a binary citric acid water solution under the same conditions (Lienhard et al., 2012), we calculated $\Delta n \approx -2.4 \times 10^{-3}$. This change is mainly due to photochemically produced CO$_2$; see a quantitative analysis in the Section 2.4.1 including remarks about the speciation of Fe.

For the slower processes (ii) and (iii), we assume that the wavelength shift is only due to the size change of the particle, and Eq. 2.1 simplifies to

$$r(t) = \frac{\lambda(t)r_0}{\lambda_0}. \tag{2.3}$$

Neglecting changes in particle density, we treat the volume change to be equivalent to the mass change (see the discussion in Section 2.4.2). The particle mass remaining ratio after time $t$ is

$$\frac{m(t)}{m_0} = \left\{r(t) / r_0\right\}^3, \tag{2.4}$$

with the initial particle mass after process (i) taken as $m_0$ to scale the mass. The mass response of the particle due to H$_2$O uptake—driven by the water activity change following CO$_2$ production—and the subsequent CO$_2$ evaporation can be calculated from the resonance shift data of Figure 2.1. The mass-change contribution due to either water uptake or CO$_2$ loss is shown in Figure 2.2 as the blue and orange lines, respectively.

For both species (CO$_2$ and H$_2$O), the diffusion equation reads

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial r^2}, \tag{2.5}$$

where $c$ is the concentration and $D$ is the diffusion coefficient. We assume CO$_2$ is uniformly distributed in the particle at $t = 0$. We solve Eq. 2.5 assuming $r = \text{const}$ because the amounts of CO$_2$ loss and H$_2$O uptake are small, further implying that these changes do not change the diffusion coefficients. We further neglect any subsequent loss of H$_2$O due to changes in water activity caused by CO$_2$. Under these assumptions, an analytical solution of Eq. 2.5 exists, yielding the total amount of each species leaving or entering the particle at any time (Crank, 1975):

$$\frac{\Delta m_s(t)}{\Delta m_s(t = \infty)} = 1 - \frac{6}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{p^2} e^{-D_s p^2 \pi^2 t / r_0^2}, \tag{2.6}$$

where $D_s$ is the diffusivity and $\Delta m_s(t = \infty)$ is the total amount of the species, $s$, lost or gained by the particle after reaching equilibrium. The particle mass changes with time due to both processes as

$$m(t) = m_0 + \Delta m_{H_2O}(t) - \Delta m_{CO_2}(t). \tag{2.7}$$
Figure 2.2: Response of the normalized mass of the particle to the first irradiation calculated from the data of Figure 2.1. Black data points are during the loss of CO$_2$ and the gain of H$_2$O. Red line: regression curve to Eq. 2.8, which allows the separation of CO$_2$ loss and H$_2$O gain. Orange line: particle mass change due to CO$_2$ loss. Blue line: particle mass gain by H$_2$O uptake, assuming a constant CO$_2$ concentration during water uptake and neglecting the subsequent loss of water together with the CO$_2$ evaporation.

Substituting Eq. (2.6) into Eq. (2.7) results in

\[
m(t) = m_0 + \Delta m_{\text{H}_2\text{O}}(t = \infty) \left\{ 1 - \frac{6}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{p^2} e^{-D_{\text{H}_2\text{O}} p^2 \pi^2 t / r_0^2} \right\} \\
- \Delta m_{\text{CO}_2}(t = \infty) \left\{ 1 - \frac{6}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{p^2} e^{-D_{\text{CO}_2} p^2 \pi^2 t / r_0^2} \right\}.
\]  

(2.8)

A best fit to Eq. 2.8 yields the diffusivities for both CO$_2$ and H$_2$O (summarized in Table 2.1). For 37% RH, we note that $D_{\text{H}_2\text{O}}$ is one order of magnitude higher than $D_{\text{CO}_2}$. Previous data of water diffusivity for highly supersaturated conditions state an uncertainty of a factor of three (Lienhard et al., 2015) or two (Davies and Wilson, 2016), respectively. Here we estimate an uncertainty of 12%, at least a factor of about four times smaller than previous measurements.

Experiments at 25 and 0% RH are shown in Figure S2.4 and Figure 2.3. For the experiment at nominally 0% RH, two irradiation pulses were used each 10 s in duration. Again, $\lambda$ decreases (blue shift); however, the amplitude of the shift is much smaller for the
2.3. Results and discussion

Figure 2.3: Temporal evolution of Mie resonance wavelength (black), refractive index (blue), and calculated normalized mass remaining (black) in the particle during photochemistry at 0% RH and 293 K. Initial particle size: 8.52 µm. Orange lines: irradiation #1 and #2, duration 10 s, ca. $470^{+740}_{-240}$ W cm$^{-2}$. Dotted gray line: equilibrated wavelengths after the last irradiation. Red line: fitting for mass data when $t > 0$.

second irradiation. As before, the apparent instantaneous blue shift (see Section 2.4.1 for time-resolved data) is attributed to refractive index change. The slower decrease in $\lambda$ after irradiation is due to the CO$_2$ loss. It is important to note that no red shift due to H$_2$O uptake was observed at RH= 0%. Under these conditions, hardly any water is present in the particle; on the contrary, the particle is still slowly losing residual water; see Figure 2.4 and its discussion below. (Note that the data shown in Figure 2.3 have been corrected for the residual water loss; see Section 2.4.3). Again, we utilize Eq. 2.8 for deducing CO$_2$ diffusivity (see Table 2.1).

To derive concentration-dependent water diffusion, we dried the particle prior to the pulsed irradiation experiment while observing its size change over time. We apply a liquid-phase diffusion model (Zobrist et al., 2011) and compare this with observations in Figure 2.4. The particle continually shrunk when RH decreased over time. The diffusion model simulates the size decrease well using the optimized water activity dependence of $D_{H_2O}$ shown in Figure 2.4. We note that our experiment is only sensitive to diffusivities of water $\lesssim 10^{-13}$ m$^2$ s$^{-1}$. Therefore, we are limited to a water activity range of 0 to 0.25. We estimate a conservative uncertainty in $D_{H_2O}$ to be within a range of a factor of 5.

Putting the newly measured diffusivity data for CO$_2$ and H$_2$O into context, we show
Figure 2.4: (a) Measured and modeled particle size change with time during the drying process, left axis. Relative humidity inside EDB, right axis. (b) Residuals between simulated and measured particle sizes. (c) Simulated citric acid concentration inside the particle during the drying process. (d) Parametrization of $D_{H_2O}$ as a function of water activity.
2.3. Results and discussion

Table 2.1: Summary of diffusivities of H$_2$O and CO$_2$ at different relative humidities.

<table>
<thead>
<tr>
<th>RH [%]</th>
<th>$D_{H_2O}$ [m$^2$ s$^{-1}$]</th>
<th>$D_{CO_2}$ [m$^2$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>$(2.59 \pm 0.31) \times 10^{-13}$</td>
<td>$(2.21 \pm 0.26) \times 10^{-14}$</td>
</tr>
<tr>
<td>25</td>
<td>$(2.1^{+1.6}_{-1.4}) \times 10^{-14}$*</td>
<td>$(5.01 \pm 0.73) \times 10^{-15}$</td>
</tr>
<tr>
<td>3$^+7$</td>
<td>$(2.3^{+5.0}_{-1.6}) \times 10^{-17}$*</td>
<td>$(2.19 \pm 0.24) \times 10^{-16}$</td>
</tr>
</tbody>
</table>

* Data obtained from the simulated particle size decrease rate during the drying process.

$D_{CO_2}$ and $D_{H_2O}$ for both photochemical and drying experiments as a function of water activity in Figure 2.5 together with S-E estimations for CO$_2$ diffusivity and literature data for H$_2$O diffusivity in binary aqueous citric acid. Diffusivities of CO$_2$ (Díaz et al., 1987) and H$_2$O (Holz et al., 2000) in pure water are roughly the same as indicated, with water self-diffusion 15% faster than CO$_2$ diffusion. Our measurement for the water activity, $a_w = 0.37$, shows that $D_{H_2O}$ is one order of magnitude larger than $D_{CO_2}$. At $a_w = 0.25$, the diffusivity of water is still larger, but only by a factor of four. For the measurement at nominally $a_w = 0$ (Figure 2.3), $a_w$ inside the particle shows a strong radial gradient (Figure 2.4c). This is due to a highly concentrated particle surface layer with very low diffusion, effectively trapping water in its interior. As a result of this gradient, we conservatively attribute the $D_{CO_2}$ to the $a_w$ range from 0 to 0.1. It is evident from our data that $D_{H_2O}$ is less than $D_{CO_2}$ by about an order of magnitude when $a_w < 0.05$. This is evidence for a crossover of $D_{CO_2}$ and $D_{H_2O}$ in aqueous citric acid/Fe$^{III}$(Cit) mixtures, occurring at $a_w \approx 0.2$, with water diffusion faster in more dilute solutions and CO$_2$ diffusion faster than water diffusion in highly concentrated viscous solutions.

Diffusivities for CO$_2$ derived from viscosity measurements (Marshall et al., 2016; Song et al., 2016) using the Stokes-Einstein relationship are shown in Figure 2.5 in comparison with our values. For $a_w > 0.15$, our measured CO$_2$ and H$_2$O diffusivities agree with the S-E. Under very dry conditions ($a_w < 0.15$), S-E estimations for CO$_2$ are about one order of magnitude smaller than our measurements, consistent with the failure of S-E predictions for highly viscous systems previously discussed (Bastelberger et al., 2017; Power et al., 2013). The newly determined $D_{H_2O}$ values for $a_w < 0.25$ are larger than extrapolations from data taken at a lower temperature (Lienhard et al., 2014) but smaller than the data for the water diffusivity of Davies and Wilson (Davies and Wilson, 2016), who used a Raman isotope technique. Presently, the reason for this discrepancy is not known; it may be due to the presence of the iron citrate complex lowering the water diffusivity.

The cause of the crossover of H$_2$O and CO$_2$ diffusivities observed under dry conditions may be due to different molecular interactions. In highly concentrated amorphous citric acid, water molecules may encounter a local environment similar to crystalline citric acid monohydrate, which is the thermodynamically stable form. Water molecules may become more bound to the citric acid network under these circumstances, whereas the same does not occur for CO$_2$. Given the large uncertainties in the viscosity data at low RH, it is conceivable that CO$_2$ follows the S-E relationship over the entire water activity range at
Figure 2.5: Diffusivities of CO\textsubscript{2} and H\textsubscript{2}O as a function of water activity in Fe\textsuperscript{III}Cit/citric acid solutions. Solid circles: this work. Dashed black line: H\textsubscript{2}O diffusivity extrapolated from data taken at lower temperature (Lienhard et al., 2014). Blue and green crosses and lines and green shading: CO\textsubscript{2} diffusivity estimated from the S-E prediction using citric acid aqueous particle viscosity data (Marshall et al., 2016; Song et al., 2016). Gray circles: H\textsubscript{2}O diffusivity measured with isotopic exchange in citric acid droplets by Davies and Wilson (Davies and Wilson, 2016). CO\textsubscript{2} and H\textsubscript{2}O diffusivities in pure water (Díaz et al., 1987; Holz et al., 2000) are shown as colored open circles ((1.77 and 2.02) \times 10^{-9} \text{ m}^{2} \text{s}^{-1}, respectively).
this temperature and the observed crossover is just due to water diffusivity deviating from S-E at intermediate RH.

For atmospheric applications, let us compare the characteristic diffusion time to reach equilibrium based on the CO$_2$ diffusivity under dry conditions. According to our data, it will be on the order of 100 s for a 200 nm particle, which is fast compared with typical chemical aging times. Please note that these considerations may change at lower temperatures, where diffusivity typically follows an Arrhenius behavior, with a large diffusion activation energy resulting in a significantly smaller diffusivity (Bastelberger et al., 2017). The methodology developed here should be applicable to more complex atmospheric particles as long as there is no other significant photochemistry occurring.
2.4 Supporting Information

2.4.1 Rapid refractive index change

In Figure S2.1 we show a close-up of the rapid blue shift in resonance wavelength of the pulsed irradiation experiment under dry conditions. First, the amplitude of the shift during irradiation, $\Delta \lambda = -0.520 \text{ nm}$ may be compared to a theoretical prediction based on ideal mixing assumptions. For simplicity, let us assume that there is no water present in the particle under dry conditions and that its density, $\rho_p$, is that of citric acid (Lienhard et al., 2012), i.e. $\rho_p = 1.58056 \text{ g cm}^{-3}$. According to reactions R1 and R2, after irradiation and before CO$_2$ loss to the gas phase, the density of the particle will decrease due to the produced CO$_2$ and the decarboxylated product (here we assume that the C$_5$ product is 3-oxoglutaric acid). Ideal mixing predicts a density change $\Delta \rho = -(7.06 \pm 0.40) \times 10^{-3} \text{ g cm}^{-3}$ using the known molar ratio of Fe$^{\text{III}}$(Cit) to citric acid (0.05), a molar volume for CO$_2$ of 34.2 cm$^3$ mol$^{-1}$ (Harvey et al., 2005) and a molar volume for C$_5$ of $(98.9 \pm 0.5) \text{ cm}^3$ mol$^{-1}$ (ChemSpider). A reduction in density alone would lead to a red shift in resonance wavelength. However, the Lorentz-Lorenz relation (Born and Wolf, 1980) allows us to calculate the corresponding change in refractive index in terms of the refractivity, $a$, of the solution:

$$n^2 = \frac{1 + 2a}{1 - a},$$

(S2.1)

$a$, to a good approximation, is a linear superposition of the molar refractivities $A_i$ (Born and Wolf, 1980):

$$a = \frac{\rho_p}{M_p} \sum_i x_i A_i,$$

(S2.2)

where we take $A_{\text{cit}} = 36.3 \text{ cm}^3 \text{ mol}^{-1}$ (Lienhard et al., 2012), $A_{\text{CO}_2} = 6.64 \text{ cm}^3 \text{ mol}^{-1}$ (Birch, 1991), $A_{\text{C}_5} = (28.4 \pm 0.3) \text{ cm}^3 \text{ mol}^{-1}$, $x_i$ is molar fraction of species $i$, and $\rho_p/M_p$ is the molar density of the mixture. This calculation yields $\Delta n = -(3.68 \pm 0.36) \times 10^{-3} \text{ nm}$. Putting $\Delta n$ and $\Delta \rho$ into Eq. 2.1 yields a resonance wavelength shift of $\Delta \lambda = -(0.53 \pm 0.21) \text{ nm}$. It is important to note that the second irradiation led to an additional rapid shift in the experiment, see Figure 2.3 of about $\Delta \lambda = -0.120 \text{ nm}$. The combined observed shift of $\Delta \lambda = -0.640 \text{ nm}$ compares favourably with the predicted shift based on ideal mixing.

We conclude that the rapid shift observed in our experiments is due to the combined effect of density and refractive index change caused by the production of CO$_2$ through the rapid decarboxylation of the Fe$^{\text{III}}$(Cit) complex upon irradiation.

In addition to the amplitude of resonance wavelength change, we also resolve the decay time of the blue shift $\tau = (2.20 \pm 0.18) \text{ s}$, see Figure S2.1 The rate of formation of •Cit can be written as (Seinfeld and Pandis, 2006):

$$\frac{d[^{\cdot}\text{Cit}]}{dt} = \phi_j[^{\text{Fe}^{\text{III}}}(\text{Cit})],$$

(S2.3)

where $j$ is the first-order rate constant for photolysis or the so-called absorption rate of
Fe^{III}(Cit), and $\phi$ is the quantum yield of reaction \( R_1 \). Assuming that reaction \( R_1 \) is followed by reaction \( R_2 \) instantaneously, then the rate of formation of CO$_2$ is the same as the one of the radical \( \cdot \text{Cit} \) (Seinfeld and Pandis, 2006):

$$
\frac{d[\text{CO}_2]}{dt} = \phi j [\text{Fe}^{III}(\text{Cit})].
$$  \hfill (S2.4)

Since the resonance wavelength shift is due to the refractive index change caused by the formation of CO$_2$, the time constant, $\tau$, can be related to the formation rate of CO$_2$ as:

$$
\tau = \frac{1}{\phi j}.
$$  \hfill (S2.5)

On the other hand, $j$ is determined by the absorption cross section of Fe$^{III}$(Cit), $\sigma$, and the photon flux, $I$ (Seinfeld and Pandis, 2006):

$$
j = \sigma I.
$$  \hfill (S2.6)

Substituting Eq. (S2.6) into Eq. (S2.5) results in

$$
\tau = \frac{1}{\phi \sigma I}.
$$  \hfill (S2.7)

With the laser intensity used in this experiment of $470^{+740}_{-240}$ W cm$^{-2}$, the photon flux $I$ is calculated to be $1.1^{+1.8}_{-0.6} \times 10^{21}$ cm$^{-2}$ s$^{-1}$ for the wavelength (473 nm) used in the experiment and the observed $\tau = (2.20 \pm 0.18)$ s. The derived absorption cross section of Fe$^{III}$(Cit) is $\sigma = 4.1^{+5.8}_{-2.7} \times 10^{-22}$ cm$^2$, assuming a quantum efficiency of $\phi = 1$. This cross section corresponds to a molar absorption of $0.11^{+0.15}_{-0.07} \text{ M}^{-1} \text{ cm}^{-1}$. [Pozdnyakov et al., 2012] mea-

Figure S2.1: An exponential decay fitting for the 10 s irradiation period at 0% RH.
sured the absorption spectra of Fe$^{III}$(Cit) in aqueous solution, yielding an approximately 500 times larger molar absorption of 60.7 M$^{-1}$ cm$^{-1}$ at 473 nm. This difference may be due to low quantum yield, which has been observed, for example, to be as low as 0.05 at 436 nm for the mono(malato)-ferrate complex (Weller et al., 2013). Partly it could be due to not all available iron being present as the Fe$^{III}$(Cit) complex. According to reported equilibrium constants (Martell and Smith, 1982; Smith and Martell, 1976), only about 25% of Fe$^{III}$ is in Fe$^{III}$(Cit) in our system. We also note that this method to deduce quantum yield is rather indirect.

2.4.2 Mass-loss retrieval considering density and refractive index change during loss of CO$_2$

![Figure S2.2: Normalized mass ratio profile of the particle at 0% RH and 293 K. Black data repeat the data of Figure 2.3, neglecting density and refractive index change due to loss of CO$_2$. Grey data: taking into account refractive index and density change, assuming ideal mixing. Grey dotted line marks the initial ratio.](image)

Using the same ideal mixing approach detailed in Section 2.4.1 above, we can account for density and refractive index changes during CO$_2$ loss in an iterative procedure. The ideal mixing approach should yield reliable estimates for the data of the irradiation experiment under dry conditions, as we may safely ignore changes due to water activity there. Figure S2.2 shows that this yields a significantly larger amplitude for the normalized mass ratio, but does not have a significant effect on the characteristic diffusion time. This supports our initial simplification of ascribing all changes in resonance wavelength shift to size changes only for the purpose of retrieval of characteristic diffusion times. The mass ratio observed under ideal mixing assumptions yields a 2% change whereas we expect a 1% change based on the initial Fe$^{III}$(Cit) to citric acid ratio. This difference may be partly
due to partial reduction of Fe$^{\text{III}}$ to Fe$^{\text{II}}$ during preparation of the solution prior to the injection of a particle into the EDB, partly due to our ideal mixing assumption and the neglect of residual water.

### 2.4.3 Raw data of the experiment under dry conditions

In Figure S2.3 we show the raw data of the irradiation experiment under dry conditions. Two things are evident from this graph. First, there is slow, residual water loss after more than two days of drying, consistent with Figure 2.4. Second, after irradiation the shift of resonance wavelength with time increases significantly, indicating faster diffusivity of CO$_2$ compared to that of H$_2$O. The data of Figure 2.3 have been corrected by subtracting a linear fit to the last 25,000 s of the data shown here in Figure S2.3.
2.4.4 Experiment at 25% relative humidity

For completeness, we show in Figure S2.4 the normalized mass data of the experiment at 25% RH together with the linear regression curve to deduce CO$_2$ diffusivity. Similar to the experiment at nominally 0% RH, we do not observe significant water uptake here. The particle was irradiated for four times with each one lasting 3 s.
Chapter 3

Photochemical degradation of iron(III)-citrate/citric acid aerosol quantified with single, levitated particle experiments

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Abstract

Iron(III) carboxylate photochemistry plays an important role in aerosol aging, especially in the lower troposphere. This complex can absorb light over a broad wavelength range, inducing the reduction of iron(III) and the oxidation of carboxylate ligands. In the presence of O$_2$, ensuing radical chemistry will likely lead to more decarboxylation, and the production of •OH, HO$_2$•, peroxides, and oxygenated volatile organic compounds, contributing to further particle mass loss. The •OH, HO$_2$•, and peroxides in turn allow the re-oxidation of iron(II) to iron(III), closing this photocatalytic cycle. In a cold and/or dry atmosphere, organic aerosol particles tend to attain highly viscous states. While the impact of reduced mobility of aerosol constituents on dark chemical reactions has received substantial attention, studies on the effect of high viscosity on photochemical processes are scarce. We choose iron(III)-citrate photochemically induced citric acid degradation as a model system to investigate how transport limitations influence photochemical processes. A multilayered photochemical reaction and diffusion (PRAD) model that includes chemical reactions and transport of each species was developed. While iron(III)-citrate photochemistry has been well established, some specific chemical reaction rates, most of the equilibrium constants of iron(III) or iron(II) citrate complexes, and the diffusivity of each species in aqueous citric acid solutions are still poorly constrained. In order to determine some of the ill-constrained parameters in the model, such as the diffusivity of O$_2$ in citric acid solution
and the re-oxidation rate of iron(II)-citrate with O\(_2\) directly, we conducted several experiments with single particles levitated in an electrodynamic balance. The results helped us either to derive the parameters directly or to establish a best-fit parameters set by tuning the model.

### 3.1 Introduction

Aerosol aging, which refers to physical and chemical transformations of atmospheric particles, plays a significant role in the impact of aerosols on climate, air quality and human health (Seinfeld and Pandis, 2006). Out of many particle types in the atmosphere, aqueous solution particles are the dominant form, in which photochemistry and radical reactions are the main drivers of chemical conversions (Bateman et al., 2011; George et al., 2015). Compared to the uptake of oxidants (e.g., \(\cdot\)OH, O\(_3\)) from the gas phase, which can be surface accommodation limited (Berkemeier et al., 2016; Davies and Wilson, 2015; Shiraiwa et al., 2011), photochemically active radiation hits the entire volume of aerosol particles, generating radicals throughout their bulk. In the lower troposphere, where UV light intensity with wavelength sufficient to directly photolyze aerosol components is low, indirect photochemistry (catalyzing redox processes of non-absorbing molecules) is especially relevant. Important indirect photochemical processes are initiated by either transition metal complexes or photosensitizers, both acting as photocatalysts for aerosol oxidation (George et al., 2012, 2015). Here, we will focus on iron(III) carboxylate catalyzed photochemistry due to the abundance and reactivity of iron(III) carboxylate in the atmosphere (Deguillaume et al., 2005).

Iron, mainly from mineral sources (soil dust or mineral fly ash), is the most abundant trace metal in the earth’s crust. By wind erosion, as well as anthropogenic emissions (e.g., traffic and combustion processes), iron enters the troposphere in particulate form, and can be incorporated into aquatic atmospheric systems during long-range transport (Deguillaume et al., 2005). Recently, Matsui et al. (2018) reported that anthropogenic combustion iron, as a source of soluble iron, has been underestimated in the past, it contributes more to the atmospheric soluble iron than dust and biomass burning sources. In the atmospheric aqueous particle phase, iron concentration can vary from \(10^{-9}\) to \(10^{-3}\) mol L\(^{-1}\) in cloud and raindrops, which is generally much higher than those of other transition metals (Hoigné et al., 2012). Depending on pH value, ionic strength and concentration of involved substances, iron can combine with organic or inorganic ligands to form iron complexes (Deguillaume et al., 2005). Dissolved iron in atmospheric aerosol particles normally exists in oxidation state (III) or (II), and one form can convert into the other, called redox cycling. One of these redox processes is the photoreduction of iron(III) to iron(II), during which ligands bound to iron(III) can be decomposed (Pozdnyakov et al., 2008; Wang et al., 2012; Weller et al., 2014; Weschler et al., 1986), or oxidized for inorganic ligands such as SO\(_3^{2-}\) (Brandt and van Eldik, 1995; Weschler et al., 1986). Here, we choose iron(III)-citrate (Fe\(^{III}\)(Cit)) in aqueous citric acid as the model system to investigate such processes in detail and in particular the effect of kinetic transport limitations in the condensed phase.
under dry conditions.

Citric acid (CA) has been identified to be an ubiquitous organic compound in ambient particles (Decesari et al., 2006; Jung and Kawamura, 2011), and therefore has been frequently used as a proxy substance for the water soluble organics in atmospheric aerosol particles (Corral Arroyo et al., 2018; Davies and Wilson, 2015; González Palacios et al., 2016; Gržinić et al., 2015; Murray, 2008; Murray et al., 2010). The thermodynamic properties of aqueous citric acid have been studied in detail by Lienhard et al. (2012), water diffusivity is known down to highly viscous solutions (Lienhard et al., 2014), and its viscosity has been recently reported (Marshall et al., 2016; Song et al., 2016). The Fe$^{III}$(Cit) complex speciation is well established (Mentasti, 1979; Silva et al., 2009), as well as the Fe$^{III}$(Cit) complex photochemistry in both solution (Abida et al., 2012; Faust and Zepp, 1993; Pozdnyakov et al., 2012) and solid states (Abrahamson et al., 1994). The catalytic cycle of Fe$^{III}$(Cit) complex in aqueous citric acid particle is represented in Figure 3.1a, and the main chemical reactions in the Fe$^{III}$(Cit)/CA aqueous system with literature rate coefficients are listed in Table A.2, together with reported equilibrium constants. Fe$^{III}$ forms a stable complex with citric acid, which absorbs light up to about 500 nm (as shown in Figure 3.1b). Excitation of Fe$^{III}$(Cit) complex induces a ligand-to-metal charge transfer (LMCT), followed by immediate decarboxylation of the central carboxyl group (reactions R1 and R2), since the hydroxyl group adjacent to a carboxyl group facilitates decarboxylation (Weller et al., 2013). The ensuing peroxy radical chemistry (in presence of O$_2$) will likely lead to more decarboxylation, peroxides and oxygenated volatile organic compounds (OVOC) production (e.g., acetone) (reactions R3–R5 and R11–R15). The *OH, HO$_2^*$, and peroxides in turn allow the re-oxidation of Fe$^{II}$ to Fe$^{III}$ (reactions R6–R10), closing this photocatalytic cycle, which is potentially an important sink of organic acids in the troposphere.

In a cold and/or dry atmosphere, aerosol particles enriched in organics tend to transit into supersaturated solutions attaining viscous, amorphous semi-solid, or even glassy states (Shiraiwa et al., 2017, Virtanen et al., 2010; Zobrist et al., 2008, 2011). These highly viscous materials are characterized by a strongly or a completely halted mobility of solutes with important consequences for physical and chemical processes (Davies and Wilson, 2015; Gržinić et al., 2015; Koop et al., 2011; Kuwata and Martin, 2012; Shiraiwa et al., 2011; Steimer et al., 2014). In turn, aerosol aging processes potentially change the viscosity (Hosny et al., 2013). Particle phase oxidation and dimerization or oligomerization increase O/C ratio as well as molar mass, which increase the viscosity and correspondingly lower the diffusivity (Shiraiwa et al., 2014). Strong diffusion limitation in high viscosity aqueous aerosol extends the equilibration time of semi-volatile secondary organic matter gas-particle partitioning (Shiraiwa and Seinfeld, 2012) and slows down the condensed phase oxidation processes (Gallimore et al., 2011; Kuwata and Martin, 2012; Slade and Knopf, 2014; Smith et al., 2002; Steimer et al., 2014; Zhou et al., 2012). For the Fe$^{III}$(Cit)/CA aqueous system, at higher viscosity, O$_2$ (as a source of *OH, HO$_2^*$, and peroxides) uptake from the gas phase and diffusivity in the particle phase will be hindered, which will slow down the Fe$^{III}$ recovery rate, and thus limit the photocatalytic cycle efficiency. To assess these effects,
a series of experiments under high viscosity (corresponding to low RH) utilizing single, micrometer size particles levitated in an electrodynamic balance have been conducted. To assess the relevance of these experimental findings under atmospheric conditions (size, irradiation, etc.), we developed a photochemical reaction and diffusion (PRAD) model to provide a detailed understanding of the interplay between chemical reaction rates and physical transport limitations. This PRAD model divides the spherical droplet into a number of shells, where equilibria, chemical reactions among all species are calculated. The transport flux of each species will then be calculated due to the formed concentration gradient. As this model requires a number of parameters unknown from literature, we performed a set of specific experiments to constrain a few of those parameters. The results from measurements and simulations will be discussed and compared, to provide a more comprehensive understanding on how transport limitations influence the reaction kinetics.

### 3.2 Experiment

#### 3.2.1 Sample preparation

Citric acid (≥ 99.5%) and Iron(III) citrate tribasic monohydrate (18–20% Fe basis) were purchased from Sigma-Aldrich. Iron (II) citrate ([Fe$^{II}$(HCit)]) were purchased from Dr. Paul Lohmann GmbH KG. Dilute aqueous solutions of Fe$^{III}$(Cit)/citric acid and Fe$^{II}$(HCit)/citric acid were made in ultrapure water (18 MΩ cm$^{-1}$, MilliQ). The molar ratio of Fe$^{III}$(Cit) or Fe$^{II}$(HCit) to citric acid was 0.05. For droplet-on-demand injection a dilute aqueous solution of about 2.5% solute weight was prepared. Since Fe$^{III}$(Cit) only dissolves slowly in water, citric acid solution with Fe$^{III}$(Cit) crystals inside has to be put in an ultrasonic bath for at least 24 hours, the same dissolving procedure was also applied to the Fe$^{II}$(HCit) powders. Note that all the procedures were done under red light illumination because Fe$^{III}$(Cit) is light sensitive (as shown in Figure 3.1b).
3.3 Photochemical reaction and diffusion (PRAD) model

3.2.2 Experimental setup

The experimental setup used in our experiments has been described in-depth previously (Steimer et al., 2015b). Briefly, an electrically charged aqueous particle is injected into an electrodynamic balance (EDB) by a droplet-on-demand generator (Hewlett-Packard 51633A ink jet cartridge filled with a dilute aqueous solution, see Sect. 3.2.1). This EDB is of the double ring design (Davis et al., 1990) with a high AC voltage applied to the two-parallel electrode rings and a DC voltage across hyperbolic endcaps. The DC field compensates the gravitational force of the particle and is adjusted automatically by a feedback loop driven by the particle’s image position on a charge-coupled device (CCD) detector to track mass changes of the particle. The chamber which hosts the balance has three glass walls, with an insulation vacuum between two outer walls and a cooling liquid (ethanol) pumped through the two inner walls, to control the temperature in the trap. The relative humidity (RH) in the chamber is regulated by adjusting the mixing ratio of a dry and humidified gas flow. Refractive index and size of spherical particles are measured by two Mie resonance spectroscopy based methods: (i) A narrow bandwidth tunable diode laser (TDL) with a scanning range of 765–781 nm is used to illuminate the particle at a scattering angle of 90°. At this angle, both transverse electric (TE) mode resonances and transverse magnetic (TM) mode resonances are measured one after the other to determine the refractive index and radius simultaneously with an accuracy of 0.005 in refractive index and a corresponding accuracy of 2 nm in size (Steimer et al., 2015b). (ii) Simultaneously, the backscatter signal from a broad-band LED centered around 640 nm is recorded using a spectrograph with a slow scan back-illuminated CCD array detector, to follow the radius change of the particle (Zardini et al., 2006). In the experiments described in this work, we used a typical total flow of 40 sccm and set the pressure inside the cell at 600 torr. The typical initial radius of the particle was \( \sim 10 \, \mu m \). For studying photochemical reactions within the levitated particle, we use a frequency doubled diode laser emitting at 473 nm (gem 473, Laser Quantum). At this wavelength, Fe^{III}(Cit) is reported to have a significant molar absorptivity of 60.7 M\(^{-1}\) cm\(^{-1}\) (Pozdnyakov et al., 2008).

3.3 Photochemical reaction and diffusion (PRAD) model

Since the observables in our experiment are bulk properties of the particle, namely mass and size changes, which do not provide specific information of chemical composition changes, the PRAD model has been developed that includes two modules: the detailed chemical processes (equilibria and chemical reactions) as well as the physical transport of all species (diffusion in the aqueous phase, and gas-particle phase partitioning). Since our experiments use particles in the 10 \( \mu m \) size range, whereas atmospheric particles are about 2 orders of magnitude smaller, a model capturing the relevant processes is needed to apply our results to atmospheric conditions.

As illustrated in Figure 3.2, a spherical droplet is divided into a number of shells, \( n \), which exchange molecules after each chemical time step. Shell thickness and numbers of shells are adjusted to enable the resolution of steep concentration gradients within an
optimal computation time. Note that we keep the volume of each shell constant instead of the thickness, so that shells become thinner and thinner from the center to the outside of the particle. In each shell and time step, we first calculate the composition using the thermodynamic equilibria of the Fe$^{III}$(Cit)/CA system, as listed in Table A.2. Then the Newton-Raphson method ([Burden and Faires] 2011) is used to calculate the products of the chemical reactions, which are also listed in Table A.2.

For the chemical reactions, a fixed time step of 0.2 s is used. After each time step of the chemical reaction calculation, liquid-phase diffusion between the shells, and the evaporation of products (or condensation of the reactant $O_2$) are computed. The time step for physical transport processes is determined dynamically to ensure both numerical stability and computational efficiency.

For each species, the molar flux from shell $i$ to the next shell $i + 1$ is calculated as

$$f_i = -4\pi r_i^2 D_l \left. \frac{dc}{dr} \right|_{r=r_i} = -4\pi r_i^2 D_l \frac{c_{i+1} - c_i}{0.5(r_{i+1} - r_{i-1})}, \quad \forall i \in \{1, 2, ..., n - 1\}, \quad (3.1)$$

where $D_l$ is the liquid phase diffusion coefficient of the corresponding species. Shell $i$ extends from $r_{i-1}$ to $r_i$, while shell $i + 1$ extends from $r_i$ to $r_{i+1}$, with $r$ being the distance from the particle center. $c$ is the molar concentration in each shell of the aqueous particle, defined as

$$c_i = \frac{N_i}{V_i}; \quad \forall i \in \{1, 2, ..., n\}, \quad (3.2)$$

where $N_i$ is moles of each species in shell $i$, and $V_i$ is the total volume of shell $i$.

At the outermost shell $n$, the gas-particle phase partitioning of each species is determined by the modified Raoult’s law. The flux from shell $n$ into the gas phase, $f_n$, is calculated to be

$$f_n = -4\pi r_n D_g \left( p_{\text{partial}} - p_{\text{vapor}} \right) \frac{RT}{}, \quad (3.3)$$

Figure 3.2: Schematic illustration of the PRAD model. Shells, transport fluxes (green arrows), and chemical processes (red arrows) of each species. The particle is radially symmetric with the surface of the particle marked as $r_n$. 
where $D_g$ is the gas phase diffusion coefficient of the corresponding species, $T$ is the temperature, and $R$ is the gas constant. $p_{\text{partial}}$ is the partial pressure of the species in the gas phase at infinite distance from the particle. Based on Henry’s law, vapor pressure of the species $p_{\text{vapor}}$ is defined as

$$p_{\text{vapor}} = \frac{c_n}{H},$$  \hspace{1cm} (3.4)

where $c_n$ is the molar concentration in the outermost shell $n$, and $H$ is the Henry’s law coefficient. Substituting Eq. (3.4) into Eq. (3.3) leads to

$$f_n = -4\pi r_n D_g \left( \frac{p_{\text{partial}}}{RT} - \frac{c_n}{HRT} \right).$$  \hspace{1cm} (3.5)

We calculate the partial pressure of $\text{H}_2\text{O}$ from RH and take the partial pressure of $\text{O}_2$ equal to the total pressure in the EDB for the experiments in which we used pure oxygen as the carrier gas (typically 600 torr). The flow rate of 40 sccm is sufficiently high to maintain $p_{\text{partial}}$ constant. For other species, $p_{\text{partial}}$ is negligible and assumed to be equal to zero. So for all species other than $\text{H}_2\text{O}$ and $\text{O}_2$, $f_n$ simplifies to

$$f_n = -4\pi r_n D_g \left( 0 - \frac{c_n}{HRT} \right) = 4\pi r_n D_g \frac{c_n}{HRT}. \hspace{1cm} (3.6)$$

Based on the calculated fluxes, moles of each species change in one diffusion time step $\Delta t$ is given by $\Delta N_i$

$$\Delta N_i = (f_{i-1} - f_i) \Delta t; \hspace{1cm} \forall i \in \{1, 2, ..., n\},$$  \hspace{1cm} (3.7)

from which the concentration and corresponding shell thickness using the molar volume of each species are recalculated for the next time step. $\Delta t$ is adjusted dynamically to ensure the concentration change in each shell is less than a threshold (3% in our calculations).

The chemical loss rate of $\text{O}_2$ is treated in the liquid phase diffusion module instead of in the chemical module, since the loss can be very fast and the life time can be smaller than $10^{-6}$ s, which means we would need to use a time step $\Delta t$ of smaller than $10^{-6}$ s if we want to calculate the $\text{O}_2$ chemical loss in the chemical module. Therefore, within each liquid phase diffusion time step, in addition to the physical transport, the chemical loss of $\text{O}_2$ molecules is calculated in each shell

$$\frac{dN_i}{dt} = -k_{\text{O}_2} N_i; \hspace{1cm} \forall i \in \{1, 2, ..., n\}. \hspace{1cm} (3.8)$$

Integration yields

$$N_i = N_i e^{-k_{\text{O}_2} \Delta t}; \hspace{1cm} \forall i \in \{1, 2, ..., n - 1\}, \hspace{1cm} (3.9)$$

where $k_{\text{O}_2}$ is total chemical reaction rate of $\text{O}_2$. In the outermost shell $n$, $\text{O}_2$ molar concentration is assumed to be at steady state all the time, meaning that the chemical loss of $\text{O}_2$ is always compensated by the condensation of $\text{O}_2$ from the gas phase

$$-k_{\text{O}_2} N_{n,\text{O}_2} = -4\pi r_n D_g \left( \frac{p_{\text{partial},\text{O}_2}}{RT} - \frac{c_n}{H_{\text{O}_2}RT} \right). \hspace{1cm} (3.10)$$
Substituting Eq. (3.2) in Eq. (3.10), we calculate the moles of \( O_2 \) in this shell, \( N_n,O_2 \), as

\[
N_n,O_2 = \frac{p_{\text{partial},O_2}}{k_{O_2}RT/(4\pi r_n D_g) + 1/(H_{O_2} V_n)}. \tag{3.11}
\]

Henry’s law coefficient of \( O_2 \) \( (H_{O_2}) \) is treated as an exponential function of water activity, \( a_w \),

\[
H_{O_2}(a_w) = H_{O_2}^0 e^{2.77(1-a_w)}, \tag{3.12}
\]

where \( H_{O_2}^0 = 1.3 \times 10^{-3} \text{ M/atm} \) \cite{sander2015}, and with the assumption that \( H_{O_2} \) is 4 times higher when \( a_w = 0.5 \), and 16 times higher when \( a_w = 0 \).

The concentration of all other species, except \( O_2 \), in the outermost shell \( n \) is either at steady state or not, depending on their respective Henry’s law coefficients. If the Henry’s law coefficient is extremely high (i.e., nonvolatile compounds), this species is not considered to evaporate from the particle phase. If the Henry’s law coefficient is quite small (i.e., volatile compounds), the evaporation rate can be fast enough to keep the concentration of this species in the outermost shell \( n \) always at steady state, which means

\[
f_{n-1} = f_n, \tag{3.13}
\]

that is,

\[
-4\pi r_{n-1}^2 D_l \frac{c_n - c_{n-1}}{0.5(r_n - r_{n-2})} = 4\pi r_n D_g \frac{c_n}{HRT}. \tag{3.14}
\]

From Eq. (3.14), \( c_n \) can be deduced to be

\[
c_n = \frac{c_{n-1}}{1 + 0.5(r_n - r_{n-2})r_n D_g/(HRT r_{n-1}^2 D_l)}. \tag{3.15}
\]

And the number of molecules of the volatile species in the outermost shell \( n \) as

\[
N_n = c_n V_n. \tag{3.16}
\]

There are several assumptions and approximations made to adapt this model to the aqueous Fe(III)(Cit)/CA system:

1. The \( D_l \) coefficient for each species is first estimated from the literature and then tuned according to our experimental results.

2. The \( D_g \) coefficient for each species \( j \) is approximated via its molar mass \( (M_j) \) compared to that of water \( (M_{H_2O}) \),

\[
D_g = D_{H_2O} \sqrt{\frac{M_{H_2O}}{M_j}}. \tag{3.17}
\]

with

\[
D_{H_2O} = 0.211 \left( \frac{T}{T_0} \right)^{1.94} \left( \frac{p_0}{p} \right), \tag{3.18}
\]

where \( T_0 = 273.15 \text{ K} \), \( p_0 = 1013.25 \text{ mb} \), and \( D_{H_2O} \) in \( \text{cm}^2 \text{ s}^{-1} \) \cite{pruppacher}.
3.3. Photochemical reaction and diffusion (PRAD) model

3. We set water activity in the particle phase always in equilibrium with the gas phase, since the RH of gas phase does not change during each experiment.

4. The bulk accommodation coefficients of all species are assumed to be 1.

5. Neglecting the influence of Fe\textsuperscript{III}(Cit), the water activity is taken from that of CA ($a_{w}^{CA}$), which has been determined by Lienhard et al. (2012)

$$a_{w}^{CA} = \frac{1 - W_{CA}}{1 + q \cdot W_{CA} + r \cdot W_{CA}^2},$$

(3.19)

with

$$q = -3.16761 + 0.01939T - 4.02725 \times 10^{-5}T^2,$$

(3.20)

and

$$r = 6.59108 - 0.05294T + 1.06028 \times 10^{-4}T^2,$$

(3.21)

where $T$ is the temperature of the system and $W_{CA}$ is the mass fraction of CA.

The water activity of citrate ($a_{w}^{Cit}$) is calculated using the same equation

$$a_{w}^{Cit} = \frac{1 - W_{Cit}}{1 + q \cdot W_{Cit} + r \cdot W_{Cit}^2},$$

(3.22)

where the mass fraction of citrate $W_{Cit}$ is treated in two fractions: citrate without Fe and citrate containing Fe. The water activity of an aqueous 1 M Fe\textsuperscript{III}(Cit) solution was determined using a water activity meter (AquaLab water, Model 3B, Decadon Device, USA) at room temperature. We found this water activity corresponds to that of a 0.81 M aqueous CA solution. Therefore, in the model, all iron containing citrate complexes (no matter Fe\textsuperscript{II} or Fe\textsuperscript{III}) are counted as 0.81 times of the corresponding citrate molarity. Then the total citrate mole amount is

$$n_{Cit}^{*} = n_{Cit} + 0.81n_{FeCit},$$

(3.23)

$W_{Cit}$ turns out to be

$$W_{Cit} = \frac{M_{Cit} \cdot n_{Cit}^{*}}{M_{Cit} \cdot n_{Cit}^{*} + M_{H_{2}O} \cdot n_{H_{2}O}},$$

(3.24)

where $M_{Cit}$ is assumed to be equal to the molar mass of CA, which is 192 g/mol. For other species $j$, the contribution to the water activity is proportional to their molar volumes ($MV$):

$$a_{w} = a_{w}^{CA} + a_{w}^{Cit} + \frac{MV_{H_{2}O}}{MV_{H_{2}O} + \sum_{j} MV_{j}},$$

(3.25)

6. The product of Fe\textsuperscript{III}(Cit) photolysis, C\textsubscript{5}, half of it is assumed to be photosensitive, producing CO\textsubscript{2} and C\textsubscript{4}, which is also assumed to photosensitive, as reactions
3.4 Results and discussion

In total, the PRAD model includes 13 equilibria and 17 chemical reactions among 32 species, as well as their condensed phase diffusivities and Henry’s law coefficients. Some of these parameters can be found in the literature, while others are not known and difficult to estimate. For instance, there are no data reported of the diffusivity of O$_2$ in citric acid solutions (at different water activities), and only little data of the chemical reaction rate of the Fe$^{II}$-citrate complex directly oxidized by O$_2$ (Gonzalez et al., 2017). In order to find the optimal parameter set, we need experimental data taken under well-controlled conditions. The model can help us understand how transport limitations affect photochemical processes in our experiments and further allow us to estimate photochemical degradation of organics under atmospheric conditions.

3.4.1 The determination of recovery rate by O$_2$

We designed a dedicated experimental procedure as shown in Figure 3.3 to determine the re-oxidation rate of Fe$^{II}$. At the beginning, we exposed a newly injected Fe$^{III}$(Cit)/CA aqueous particle to blue laser irradiation (473 nm, 4 W cm$^{-2}$) in pure N$_2$ for 500 s until all Fe$^{III}$ was reduced through photolysis reactions R1 and R2 (listed in Table A.2). Then we turned off the irradiation and switched gas flow from N$_2$ to O$_2$ (note: in total it took about 30 min until the trap was filled with O$_2$), inducing the production of reactive oxygen species (ROS) (R3–R5). Fe$^{II}$ is oxidized back to Fe$^{III}$ either by ROS (R6–R9) or directly by O$_2$ (R10) in the dark. After waiting for a certain recovery time period in O$_2$, we switched the gas flow back to N$_2$ and repeated the photolysis step. The value of a Mie resonance wavelength decrease during the second irradiation period normalized to the value in the first irradiation period indicates the ratio of Fe$^{III}$ recovered in O$_2$ in the dark (assuming the first irradiation started with 100% Fe$^{III}$, which might not be the case since partial Fe$^{III}$ was reduced during sample preparation). We repeated the photolysis procedure for several times, and between each irradiation the particle was recovered in O$_2$ for different time periods. The shift of the resonance wavelength during each irradiation shows how much Fe$^{III}$ recovered in O$_2$ in the dark before that irradiation. The recovery test was conducted at 293.5 K under three different relative humidities: 24% RH, 48% RH, and 65% RH.

Figure 3.4 shows the temporal evolution of the Mie resonance wavelengths in two irradiation experiments: the black one indicates the first irradiation with a fresh Fe$^{III}$(Cit)/CA particle, and the red one is one irradiation right after the particle recovered in O$_2$ for 45 min. The particle was kept at constant temperature and relative humidity. Clearly, in both cases the resonance wavelengths decrease during irradiation, but with different shift amplitudes. According to the analysis detailed in Chapter 2 the fast shift in resonance wavelength is related to a change in refractive index, which is proportional to a change in composition and as such proportional to the fraction of photochemically active Fe$^{III}$ in the particle. Therefore, according to Figure 3.4 we conclude that the Fe$^{III}$(Cit)/CA particle
3.4. Results and discussion

Figure 3.3: Schematic of the experimental procedure to investigate the recovery efficiency under different relative humidities (24%, 48% and 65% RH). Orange columns represent laser irradiation (473 nm, 4 W cm\(^{-2}\)) in N\(_2\), each illumination takes place in a nitrogen atmosphere for a period of 500 s; grey columns mark the recovery process by O\(_2\) in the dark, here the time interval was varied. Green arrows indicate the evaporation of volatile product, CO\(_2\).

Initially had more Fe\(^{III}\) than what could be re-oxidized in O\(_2\) for 45 min. The reason is that in the fresh particle, all Fe supposedly was in Fe\(^{III}\) (which might not have actually been the case due to partial reduction of Fe\(^{III}\) during sample preparation), while after the particle has been totally photoreduced, exposure to O\(_2\) for 45 min did not re-oxidize all reduced Fe\(^{II}\) to Fe\(^{III}\). We normalize the change of \(\lambda\) with the first time irradiation of a fresh Fe\(^{III}\)(Cit)/CA particle. This allows us to determine the Fe\(^{III}\) fraction after a certain time interval of O\(_2\) recovery. The re-oxidized Fe\(^{III}\) fraction as a function of recovery time in O\(_2\) at different RH is summarized in Figure 3.5 (solid dots).

Similar tests were done by starting with freshly injected Fe\(^{II}\)(HCit)/CA particles. The only difference in experimental procedure compared to the Fe\(^{III}\)(Cit)/CA system is the first step: instead of irradiating the fresh particle in N\(_2\), we initially exposed the particle to O\(_2\) in the dark for a certain time interval, during which Fe\(^{II}\) is oxidized directly by O\(_2\) (reaction R10) and by peroxy chemistry in the following (reactions R7–R9). Afterwards, the same irradiation and recovery procedures as reported above were taken. The normalized Fe\(^{III}\) fractions are also shown in Figure 3.5 (black open circles), with two special data points from the first oxidation period of two freshly injected particles, shown as open green stars.

Let us first note that the data in Figure 3.5 show considerable scatter. Here, in contrast to what was discussed in Chapter 2, we need to analyze the normalized amplitude of the wavelength shift instead of a decay time. Any uncertainty in the normalization of an individual experiment will cause a corresponding uncertainty in the normalized wavelength shift. However, it is evident that with longer time intervals in O\(_2\), more Fe\(^{III}\) is recovered. At 48% and 65% RH, about 10 h exposure to O\(_2\) is sufficient for all Fe\(^{II}\) to be re-oxidized, while at 24% RH, the recovery even after 25 h was not yet complete, but only about 40%. This can be attributed to molecular diffusion limitations at lower RH: it takes more time for O\(_2\) to diffuse into the particle, and for Fe\(^{II}\) to diffuse out to the surface of the particle to react with O\(_2\). When the RH increases from 48% to 65%, there is no significant difference of the Fe\(^{III}\) fraction recovered with time, indicating that the recovery rate is no longer limited by molecular diffusion at 48% RH. By tuning the direct oxidation rate
Figure 3.4: Temporal evolution of two Mie resonance wavelengths shifts normalized to the wavelength prior irradiation; blue area marks the time with irradiation (473 nm, 4 W cm$^{-2}$). Black: first irradiation with a fresh Fe$^{III}$(Cit)/CA particle in N$_2$, red: irradiation right after the particle recovered in O$_2$ for 45 min. The experiment was done at 48% RH and 293.5 K.
Figure 3.5: Fe$^{III}$ fraction after different time intervals of recovery in O$_2$. Fe$^{III}$(Cit)/CA particles at 293.5 K with 24% RH (red dots), 48−49% RH (black dots), and 64% RH (blue dots). Solid green star: Fe$^{III}$(Cit)/CA particle kept in N$_2$ after the irradiation for 16 hours before switching to O$_2$ at 48% RH. Open black circles: experiments with Fe$^{II}$(HCit)/CA particles at 46−50% RH. Open green stars: fresh Fe$^{II}$(HCit)/CA particles recovered in O$_2$ before any irradiation at 46−50% RH. Lines: red (24% RH), black (48% RH), and blue (64% RH) are the Fe$^{III}$ fractions predicted using our PRAD model.
of Fe$^{II}$ by O$_2$ (R10) and the diffusivity of O$_2$, we are able to model the recovery rate at different RH using our PRAD model as shown in Figure 3.5. According to the comparison of model with the experiments, the reaction rate coefficient of R10 is 0.05 M$^{-1}$ s$^{-1}$, which is a factor of 60 smaller than the value that Gonzalez et al. (2017) estimated from their model ($3 \pm 0.7$ M$^{-1}$ s$^{-1}$). The liquid phase diffusivity of O$_2$ turns out to be $3.2 \times 10^{-17}$ m$^2$ s$^{-1}$ at 24% RH, smaller than $4.3 \times 10^{-15}$ m$^2$ s$^{-1}$ at 48%, and $2.1 \times 10^{-13}$ m$^2$ s$^{-1}$ at 65% RH, where the recovery process is limited by chemical reactions instead of the diffusivity. These diffusivities of O$_2$ are 1–2 orders of magnitude smaller than those of CO$_2$ discussed in Chapter 2. This contradicts intuition. However, we need to stress that in the model some of iron related complex equilibrium constants and the Henry’s law coefficient of O$_2$ at different water activities are uncertain as well and make a significant difference to the determination of O$_2$ solubility. If the solubility of O$_2$ would be less than what our parameters predict now, then a larger O$_2$ diffusivity would be consistent with our data. Additional constraints are needed to reduce uncertainties in this part of the parameter set of the PRAD model. In addition, as we mentioned, it took at least 30 min for O$_2$ to be filled in the trap during the gas flow switching, the life time of organic radicals needs to be reconsidered. In the PRAD model, we do not take the radical-radical self reactions (R17) into account, which may not be true in reality. The extreme case is the special data point (solid green star) shown in Figure 3.5 the particle was kept in N$_2$ for 16 hours (to make sure that no radicals exist anymore in the particle) after the irradiation before switching to O$_2$ for recovery. After 3 hours in O$_2$, it shows similar recovered Fe$^{III}$ fraction compared to ones recovered in O$_2$ right after the irradiation, indicating that radical chemistry may not be dominant in Fe$^{III}$ re-oxidation process.

3.4.2 The effect of RH on photocatalytic degradation

In the previous section, we discussed transport limitations induced by limited O$_2$ diffusivity at low RH for the re-oxidation of Fe$^{II}$ to Fe$^{III}$. These data helped constrain the parameter set of our PRAD model. Next we performed experiments with continuous irradiation at different RH in presence of O$_2$ to quantify the kinetic limitations for the complete photocatalytic cycle shown in Figure 3.1 and tested the model performance under these conditions. Expected is a continuous decrease of the particle mass and size due to the evaporation of volatile products.

The Mie resonance shift, $\Delta \lambda$, is recorded during a 5 hours exposure to laser irradiation (473 nm, 4 W cm$^{-2}$) in a pure O$_2$ gas phase and the particle radius prior to the exposure, $r_0$, is determined using high-resolution Mie resonance spectroscopy. At time $t_0$, the Mie parameter, $X$, of a specific resonance by definition is $X_0 = 2\pi r_0/\lambda_0$. If the refractive index is assumed to stay constant, the radius can be easily obtained by following the shift in resonance wavelength (Zardini et al., 2006):

$$r(t) = \frac{(\lambda_0 + \Delta \lambda(t))r_0}{\lambda_0}. \quad (1)$$

A slightly more realistic approximation on how the refractive index and density of the par-
3.4. Results and discussion

ticle changes during photocatalytic degradation is the assumption of a quasi-steady state. Here, in a simplified scheme, each photocatalytic cycle produces CO\textsubscript{2} and transforms one citric acid to C\textsubscript{5} with the CO\textsubscript{2} concentration within the particle staying constant, because of the CO\textsubscript{2} flux to the gas phase. These assumptions allow to account for refractive index and density change in a similar manner to the one explained in detail in Chapter 2 Section 2.4.2. Using ideal mixing and the Lorenz-Lorentz relationship we approximate density and refractive index during mass loss and retrieve the radius of the particle accordingly.

In order to compare the relative size changes of different particles with different initial sizes, we plot in Figure 3.6 the radius remaining ratio, i.e., the particle radius normalized to its initial radius. Let us first note, that the retrieved radius does not depend strongly on whether we assume quasi-steady state or constant density and refractive index, as the effect of density change and refractive index change almost compensate for the steady state assumptions described above.

Clearly, the particle shrinks due to the evaporation of photochemical products and the degradation progresses are faster at higher RH. At lower RH, the particle is more viscous, reducing the mobility of molecules. The products diffuse more slowly to the surface of the particle and evaporate out. More important, O\textsubscript{2} diffuses more slowly into the bulk of the particle, less HO\textsubscript{2}• and H\textsubscript{2}O\textsubscript{2} formation and hence less Fe\textsuperscript{II} can be re-oxidized, resulting in fewer photochemically active Fe\textsuperscript{III} complexes available for photocatalytic degradation. We observe that the degradation rate is quite sensitive to RH in the range of 40\% to 50\% RH, indicating that the diffusivity of O\textsubscript{2} may have a drastic change in such RH range, which has already been observed for the diffusivity of H\textsubscript{2}O (Lienhard et al., 2014) in aqueous citric acid droplet. The model simulations (Figure 3.6b) show a very similar trend and magnitude, but a generally faster degradation.

Both measurements and simulations show a consistent acceleration of degradation rate with time for all cases, most pronounced for the 50 \% RH case. Our PRAD model allows us to study the concentration profiles of the various species inside the particle. We plot the concentration profiles of four important species for the 50\% simulation in Figure 3.7, namely O\textsubscript{2}, CO\textsubscript{2}, HO\textsubscript{2}•, and C\textsubscript{4}. The particle has an initial radius of 8 \(\mu\text{m}\), which shrinks upon photochemical degradation to about 7 \(\mu\text{m}\) within 5.5 hours. Initially, photooxidation occurs throughout the entire volume of the particle, with a corresponding production of CO\textsubscript{2}. To maintain the photocatalytic cycle, O\textsubscript{2} from the gas phase needs to be resupplied by condensation on the surface of the particle, with subsequent diffusion into the bulk (see Figure 3.7a). The condensed phase diffusion limitation causes a permanent gradient in O\textsubscript{2} with more O\textsubscript{2} near the surface and less in the bulk. Essentially, the HO\textsubscript{2}• is linked to the O\textsubscript{2} concentration, resulting in a similar profile (panel b). The CO\textsubscript{2} concentration (panel c) increases initially throughout the bulk of the particle, with a gradient towards the surface, because of its loss to the gas phase. As less Fe\textsuperscript{III}(Cit) is available after the initial reduction to Fe\textsuperscript{II}, the CO\textsubscript{2} concentration decreases. Interestingly, its concentration starts to increase again and reaches another maximum at around 2 hours after the irradiation started. We attribute this phenomenon to the production of other photosensitive species, such as C\textsubscript{4} compounds. As shown in panel d, C\textsubscript{4} concentration develops a maximum between 1−2
Figure 3.6: (a) Fe$^{III}$(Cit)/CA (molar ratio 0.05) particle radius change with irradiation time (473 nm, 4 W cm$^{-2}$) at 300 K with different relative humidities: 16.5% RH (cyan), 28.5% RH (magenta), 40% RH (black), 47% RH (red), 47.5% RH (green), and 50% RH (blue). Note, that the 50% RH data show two lines, with a shaded region between them. The upper curve uses the steady state assumption for radius retrieval, the lower one assumes constant refractive index and density. (b) Corresponding radius remaining from model output.

hours, which explains the second maximum of CO$_2$ concentration through its photolysis (reactions R12 and R14). Because of the rather complex interactions between chemistry and transport of each and between species, it is difficult to identify a single cause for the acceleration observed in the model. A small part is due to the increase in Fe concentration with time (as the volatile species have been lost to the gas phase), another to our model implementation on absorption and solubility of the lower carbon number products from the ongoing photocatalytic degradation.

3.5 Conclusions and outlook

The Fe$^{III}$(Cit)/CA photochemistry system was used to investigate the effect of transport limitations on chemical reactions. The diffusivity of O$_2$ in aqueous Fe$^{III}$(Cit)/CA particle at 24%, 48%, and 65% RH are determined with the assistance of our PRAD model. However, these values still need to be optimized by evaluating the limitation from chemical reactions depending on Henry’s law coefficient of O$_2$ and relevant equilibrium constants. We observed strong kinetic transport limitations for photocatalytic degradation mostly by O$_2$ diffusivity under low RH conditions. Especially in the range of 40% to 50% RH, the cycling efficiency is quite sensitive to RH most probably due to the diffusivity of O$_2$ sensitive to RH in this range. And more model simulations should be run to find out sensitive parameters for different processes. With well-defined parameters, we can better understand the interactions between transport limitations and chemical reactions, and predict the organic aerosol aging under atmospheric conditions.
Figure 3.7: For 50% RH case, simulated (a) O$_2$, (b) HO$_2^*$, (c) CO$_2$, and (d) C$_4$ complex concentration profiles for a particle with an initial radius of 8 µm.
Chapter 4

Photocatalytic degradation of single, levitated organic aerosol particles containing iron nanoparticles or Arizona test dust


Abstract

Presently, availability of free iron from mineral dust in internally mixed aerosol containing organic matter is highly uncertain. For example, carboxylic acids are known to complex with iron, absorb light in the visible spectral region and can act as a photocatalyst. Photochemical degradation of the carboxylate ligands will lead to the re-partitioning of organic matter of the condensed phase to the gas phase. Here, we use aqueous citric acid with iron in different forms as a proxy for such internally mixed atmospheric aerosol particles. Specifically, we used micron size levitated droplets in an electrodynamic balance containing either Fe$_2$O$_3$ nanoparticles (< 50 nm) or Arizona Test Dust (ATD) particles (< 3 μm) in aqueous citric acid. As reference, we studied iron(III)-citrate dissolved in aqueous citric acid droplets at various concentrations. We observe substantial mass loss up to 80% of the initial mass over 24 hours of irradiation for the reference droplets containing dissolved iron(III)-citrate, a similar loss for the droplets containing Fe$_2$O$_3$ nanoparticles and a smaller loss for the droplets containing ATD. Comparing the time needed for a ~ 20% mass loss, we conclude that around 25% of the available iron in the droplet containing Fe$_2$O$_3$ nanoparticles is active for photocatalytic degradation, whereas only 5–12.5% of the nominal iron in ATD becomes photochemically active. Using a recently developed photochemical reaction and diffusion model, we predict photochemical degradation in accumulation mode size particles under solar irradiation, which is influenced by the transport
limitation of $O_2$, but still shows significant mass loss.

4.1 Introduction

Iron is the most abundant transition metal in the earth’s crust. Mineral dust by wind erosion is the main source of iron in the atmosphere, as well as anthropogenic activities such as industrial processes and combustion (Deguillaume et al., 2005). 1600 Tg of mineral dust are estimated to be released into the atmosphere every year (Andreae and Rosenfeld, 2008), and it contains 3.5% iron by mass on average (Jickells et al., 2005). The total iron content from rural and urban sources can vary over a large range from 10 to 1900 ng Fe m$^{-3}$ air or from 10 to 560 mg Fe g$^{-1}$ of aerosol particle mass (Weber et al., 2000). Although dust particles are primarily from arid or semi-arid regions, they can be transported over long distances, and influence air quality and human health (Kanatani et al., 2010; Usher et al., 2003). Iron reaches the atmosphere either as ‘structural iron’ trapped in the crystal lattice of aluminosilicate minerals, or as ‘free iron’ in the form of oxides (e.g., hematite (Fe$_2$O$_3$) and goethite ($\alpha$-FeOOH) from desert soils (Lafon et al., 2004), and ferrihydrites (Fe$_5$HO$_{84}$H$_2$O)) from Saharan dust (Rodriguez-Navarro et al., 2018), or sulfides (e.g., FeS$_2$, FeS and Fe$_{1-x}$S from coal combustion) (Kopcewicz and Kopcewicz, 2001). Once iron containing particles reach the atmosphere, they begin to participate in various chemical and physical processes, which can increase the availability of soluble iron in aerosol particles (Desboeufs et al., 1999; Spokes et al., 1994; Zhu et al., 1993, 1997; Zhuang et al., 1992).

As a major component in atmospheric aerosol particles, organic compounds have received more and more attention as potential ligands for iron(III) complexation. For instance, as an important fraction of water soluble organic compounds, HUmic Like Substances (HULIS) have been reported to be strong chelating ligands with iron(III), even though the composition of HULIS is not fully understood (Dou et al., 2015; Kieber et al., 2003; Okochi and Brimblecombe, 2002; Willey et al., 2000). Specifically, oxalate and other carboxylates have been identified to be important ligands for iron(III) because they are available in sufficient amount (Chebbi and Carlier, 1996; Kahnt et al., 2014; Kawamura et al., 1985), and the carboxylate groups are acidic enough to dissociate to chelate with iron(III) at atmospheric pH values (Okochi and Brimblecombe, 2002). Iron(III) carboxylate complexes are well-known photoactive compounds (Wang et al., 2012; Weller et al., 2013, 2014), which can catalyze the degradation of organics. We choose iron(III)-citrate ([Fe$^{III}$(OOCCCH$_2$)$_3$C(OH)], short Fe$^{III}$(Cit)), as a reference species. Fe$^{III}$(Cit) photochemistry is well established in both solution (Abida et al., 2012; Faust and Zepp, 1993; Pozdnyakov et al., 2012) and solid states (Abrahamson et al., 1994). It can catalyze the decarboxylation of citric acid (CA). With $O_2$ present, photoreduced iron(II) can be oxidized back to iron(III), forming a catalytic cycle, in which citric acid can be continuously degraded (Pozdnyakov et al., 2008; Wang et al., 2012).

Arizona Test Dust (ATD) particles, which is essentially ground sand from the Arizona desert, has often been used as a laboratory surrogate for natural mineral dust in the atmosphere. It has been verified that ATD mimics quite well the heterogeneous reactivity
of authentic dust samples (Crowley et al., 2010; Vlasenko et al., 2005). ATD contains a mixture of metal oxides, which are generally present in atmospheric mineral aerosols in various proportions (El Zein et al., 2013). The ATD (Powder Technology Inc.) we use contains SiO$_2$ (68–76%), Al$_2$O$_3$ (10–15%), Fe$_2$O$_3$ (2–5%), Na$_2$O (2–4%), CaO (2–5%), MgO (1–2%), TiO$_2$ (0.5–1.0%), and K$_2$O (2–5%) (Matthews et al., 2014). Iron oxide is an important component of mineral dust, and is often used as a model compound to mimic the surface reactivity of mineral aerosols. We choose Fe$_2$O$_3$ nanoparticles (<50 nm) and ATD (nominal 0–3 µm) dispersed in citric acid aqueous solution droplets, together with reference droplets with Fe$^{III}$(Cit) solutions of various concentrations in citric acid, for investigating the degradation of citric acid photocatalyzed by iron species.

4.2 Experiment

Citric acid (≥ 99.5%) and Iron(III) citrate tribasic monohydrate (18–20% Fe basis) were purchased from Sigma-Aldrich. Arizona test dust (0–3 µm) was purchased from Powder Technology Inc., and iron(III) oxide nanopowder (Fe$_2$O$_3$, < 50 nm) was obtained from Sigma-Aldrich. Dilute citric acid aqueous solution (2.5% wt) was made in ultrapure water (18 MΩ cm$^{-1}$, MilliQ). Then Fe$^{III}$(Cit), or Fe$_2$O$_3$, or ATD was added, with the molar ratio of Fe$^{III}$(Cit) to citric acid being either 0.01 or 0.05, the molar ratio of Fe$_2$O$_3$ to citric acid being 0.025, and the mass ratio of ATD to citric acid being 1, respectively. Since Fe$^{III}$(Cit) only dissolves slowly in water, citric acid solution with Fe$^{III}$(Cit) crystals inside has to be put in an ultrasonic bath for at least 24 hours. Fe$_2$O$_3$ nanoparticles or ATD particles were dispersed in citric acid solution with the assistance of the ultrasonic bath for several minutes. Note that all the procedures were done under red light illumination due to the light sensitivity of iron species.

Dilute aqueous droplets of approximately 140 pl, equivalent to a radius of about 32 µm radius, were generated using an ink-jet cartridge (Hewlett-Packard 51633A ink jet). The droplets are inductively charged upon ejection from the cartridge into an electrodynamic balance (EDB). The EDB setup has been described in-depth previously (Steimer et al., 2015b). The EDB is of the double ring design (Davis et al., 1990) with a high AC voltage applied to the two-parallel ring electrodes and a DC voltage across hyperbolic endcaps. The DC field compensates the gravitational force of the particle and is adjusted automatically to keep the particle levitated in the chamber. The chamber has three glass walls, with an insulation vacuum between two outer walls and a cooling liquid (ethanol) pumped through the two inner walls, to control the temperature in the trap. The relative humidity (RH) in the chamber is regulated by adjusting the mixing ratio of a dry and humidified gas flow. A laser emitting in the blue wavelength region (Gem 473, Laser Quantum, $\lambda$ =473 nm, 1=4 W cm$^{-2}$) allows to irradiate the particle from below for photochemical processing. Refractive index and size of spherical particles are measured by two Mie resonance spectroscopy based methods: (i) A narrow bandwidth tunable diode laser (TDL) is used to determine the refractive index and radius simultaneously with an accuracy of 0.005 in refractive index and a corresponding accuracy of 2 nm in size (Steimer et al., 2015b). (ii) Simultaneously,
a broad-band LED is used to follow the radius change of the particle (Zardini et al., 2006). Both techniques require spherical symmetry of the droplet. Once the spherical symmetry is strongly disturbed by solid inclusions (as in the case of the micron size inclusion ATD dispersion droplets), approximate sizing has been used as described by Zardini and Krieger (2009). The temperature of the experiments was 293.5 K, the pressure was set to 600 torr, total gas flow was 40 sccm and RH was set to about 50%.

4.3 Photochemical reaction and diffusion (PRAD) model

A photochemical reaction and diffusion (PRAD) model that includes the detailed chemical processes (equilibria and chemical reactions) as well as the physical transport of all species (diffusion in the aqueous phase, and gas-particle phase partitioning) in Fe(III)/(Cit)/citric acid system has been described in detail in Chapter 3. Briefly, the spherical droplet is divided into a number of shells, \( n \), that continuously exchange molecules. Shell thickness and numbers of shells are adjusted dynamically enabling the resolution of steep concentration gradients within an optimal computation time. In each shell and with a fixed time step of 0.2 s, we calculate the chemical composition accounting for thermodynamic equilibria and chemical reactions. After each time step of the chemical composition calculation, liquid-phase diffusion between the shells, and the evaporation of products (or condensation of the reactant O2) are computed. The time step for physical transport processes is determined dynamically to ensure both numerical stability and computational efficiency. With well-defined parameters, this model can be used to not only evaluate the photocatalytic role of Fe present as Fe2O3 and ATD in the aerosol particles, but also predict the degradation of organic acids in iron containing aerosol particles under various atmospheric conditions.

4.4 Results and discussion

4.4.1 Photochemical degradation in aqueous Fe(III)/(Cit)/CA droplets

For a typical experimental run on an aqueous citric acid droplet containing iron species, we first waited for around 10 hours in the dark until the droplet was in equilibrium with the constant RH and T. Permanent irradiation with the laser initiated photochemistry. Raw data of an experiment are shown in Figure 4.1. A Fe(III)/(Cit)/citric acid droplet was kept at around 52% RH and 293.6 K (panel a) during the whole experiment. The LED based Mie resonance spectra was recorded, color coded normalized intensity of wavelength versus time is shown in panel b. The radius of the particle (black curve in panel c) is derived from the shift in a specific resonance wavelength of panel b assuming constant density and refractive index, see Chapter 3 for a detailed discussion. Also, plotted in panel c is the DC voltage compensating the gravitational force and the Stokes drag force originating from the flow of gas through the EDB cell. Neglecting changes in the particle density, we treat volume change to be equivalent to mass change. To compare mass change derived from the feedback voltage and mass change derived from size estimation, we calculate a particle
Figure 4.1: Typical experimental run on a Fe$^{III}$(Cit)/citric acid (molar ratio 0.05) particle. (a) Relative humidity and temperature measured close to the droplet. (b) Color map of intensity of Mie resonance spectra measured with the LED. (c) Black line: radius of the droplet, with the initial value determined with TDL, and the change in radius determined from LED data given in (b); Orange line: DC voltage compensating gravitational force. (d) Uncorrected (grey) and corrected (black) mass remaining ratio from Mie resonance shift, and normalized mass remaining ratio from DC voltage (orange). Blue shaded region in panels a, c, and d indicates the time of laser irradiation.
mass remaining ratio, i.e.

\[
\frac{m(t)}{m_0} = \left\{ \frac{r(t)}{r_0} \right\}^3,
\]

with the initial particle mass taken as \( m_0 \). The mass remaining ratio is plotted with grey line in Figure 4.1d. Since the particle changes composition substantially during irradiation, we used a steady state assumption for the accompanying refractive index and density changes to correct the size retrieval (see Chapter 3 for details), which shows in panel d with black line. The density and refractive index changes of the particle almost compensate each other, therefore the corrected value is not significantly different from the uncorrected one. And we normalize DC voltage to initial value as relative mass change, showing in panel d with orange line. Clearly, there is a larger uncertainty with the DC measurement in general, since we do not account for the change in the drag. And our size retrieval needs quite strong assumptions. In this light we find the agreement satisfactory. Also note that there is an accelerating mass loss between 70% to 50% mass remaining ratio, which is also shown in the model simulation. We propose the assumption of the production and accumulation of other low volatile photosensitive species, facilitating the photochemical processes (discussed in detail in Chapter 3).

4.4.2 The effect of available iron

All experiments are done at 50% RH and 293.5 K over a long time scale (at least two days), as shown in Figure 4.2a. A zoomed in section of the first 35 hours are shown in panel b. Note, that all data are based on mass calculated from size retrieval assuming constant density and refractive index. Also, note that for the particles containing solid inclusions we used the size retrieval detailed in Zardini and Krieger (2009). Here, we cannot retrieve data continuously, because of the noise in the resonance spectra due to symmetry distortions caused by the inclusions. The mass remaining data show also more noise when compared to the spherical symmetric droplets containing no solid inclusions.

We found that aqueous citric acid droplets containing no iron are not photosensitive when irradiated at 473 nm. (They show even a small mass increase with time, most likely due to NH\(_3\) uptake from impurities in the gas phase.) In contrast, if iron containing complexes are added, very significant mass loss is observed due to the evaporation of CO\(_2\) and other (semi-)volatile products. The particle containing Fe\(^{III}\)(Cit) with the molar ratio to citric acid of 0.05 shows a faster mass loss rate than the one with a smaller molar ratio of Fe\(^{III}\)(Cit) (0.01). If the times are compared at which 10% mass loss was reached (10 h versus 22h), the time scale varies by a factor of about 2. The particle containing Fe\(_2\)O\(_3\) nanoparticles has a mass loss rate in between, with 10% mass loss reached in 15 h. Note that the molar ratio of Fe\(_2\)O\(_3\) to citric acid is 0.025, meaning that the molar ratio of Fe\(^{III}\) to citric acid is 0.05. If all Fe\(_2\)O\(_3\) nanoparticles would completely dissolve in aqueous citric acid—50% RH corresponds to an citric acid concentration of 6.25 M (Lienhard et al., 2012)—we would therefore expect the degradation rate to be equal to the one of the particle with the same Fe\(^{III}\)(Cit) to citric acid ratio. Also, the mass remaining after long irradiation times is significantly larger than that of particles containing Fe\(^{III}\)(Cit). The mass remaining
4.4. Results and discussion

Figure 4.2: (a) Photocatalytic mass loss observed under 473 nm irradiation for aqueous citric acid particles in O₂ at 50% RH and 293.5 K. Particles contain either dissolved Fe^{III}(Cit) (orange and red), or Fe₂O₃ nanoparticles (green), or ATD particles (blue). Pure aqueous citric acid droplet is tested as a reference (black). (b) Zoomed-in view of the blue box in (a). Dotted lines are PRAD model predictions for aqueous Fe^{III}(Cit)/citric acid particles for different molar ratios of Fe^{III}(Cit) to citric acid.

The photochemical reaction and diffusion (PRAD) model detailed in Chapter [3] is used to calculate contour lines of equivalent Fe^{III}(Cit) concentrations in panel b of Figure 4.2. These allow us to estimate the amount of dissolved Fe^{III}(Cit) that show the same degradation rate as observed for Fe₂O₃ and ATD. Just comparing the time needed for the first 15% mass loss, as shown in Figure 4.2b, we conclude that the experiment with the Fe₂O₃ nanoparticles corresponds to one with a citric acid droplet containing Fe^{III}(Cit) in a molar ratio to citric acid of 0.013. This means that about 25% of the available iron in the droplet containing solid Fe₂O₃ nanoparticles inclusions is active for photocatalytic degradation. The same consideration for the experiment with the ATD inclusions yield that only 5−12.5% of the nominal Fe^{III} in ATD is photochemically active. We have to admit that since Fe₂O₃ nanoparticles and ATD particles are not fully dissolved in the solution, there is an unavoidable uncertainty of the number of particles in the injected droplet, even though we tried to mix them well before injection.

4.4.3 Predication of photochemical aging in iron containing aerosols under atmospheric conditions

As all EDB experiments use particles in a size range about 1 to 2 orders of magnitude larger compared to those of atmospheric aerosol particles and our experiments are performed with monochromatic irradiation in a pure O₂ atmosphere, we use the PRAD model to estimate the magnitude of atmospheric photochemical degradation of organic particles.
with iron containing dust inclusions. Based on our observations in the previous section, we assume that an aqueous Fe\textsuperscript{III}(Cit)/citric acid particle with a molar ratio of 0.01 is representative for an organic particle with dust inclusions. In a simple model setting, we assume the radius of the particle to be 500 nm, RH=40%, T=293.5 K and an actinic flux of the sunlight at 0° zenith angle (Madronich et al., 1995) (12 hours irradiation reoccurring every 24 hours). Figure 4.3 shows the decrease of radius with time over three days. The particle radius decreases from 500 nm to around 430 nm (∼15% size decrease) over the entire time period. During each 12 hours irradiation period, the particle shrinks drastically due to the evaporation of CO\textsubscript{2} and other (semi-)volatile products. In the following 12 hours dark period, the size stays almost constant, with a tiny decrease due to the evaporation of semi-volatile products remaining from the last irradiation period. Note that there is a short period of acceleration of degradation at the beginning of the first irradiation, afterwards the degradation continues almost linearly with time during the irradiation, although the slope is slightly larger for the third day when compared to the second day. The acceleration in the beginning is likely due to the production of secondary photosensitive compounds (e.g., the photolysis of C\textsubscript{5} and C\textsubscript{4}: reactions R11−R15 in Table A.2), whereas the increase in the slopes from second to third day is likely due to the increase of Fe\textsuperscript{III}(Cit) concentration upon the mass loss of volatile species to the gas phase. This effect can be seen from the concentration profiles calculated with the PRAD model shown in Figure 4.4. The concentration of Fe\textsuperscript{III}(Cit) is getting higher with smaller volume, as shown in Figure 4.4d (dark red in the second dark period). During the irradiation, almost all Fe\textsuperscript{III} is photoreduced, while in the dark, Fe\textsuperscript{III} is recovered by the oxidation of O\textsubscript{2}, as shown in Figure 4.4a and b. During the irradiation, the recovery process is limited by the condensed phase diffusivity of O\textsubscript{2}, indicated by the concentration gradient of O\textsubscript{2} in Figure 4.4c. Close to the particle surface, more Fe\textsuperscript{III} is reproduced in the presence of O\textsubscript{2}, thus generating more photosensitive Fe\textsuperscript{III}(Cit) in the outer layers.

4.5 Summary and conclusions

Aqueous citric acid droplets containing dissolved Fe\textsuperscript{III}(Cit) exhibit a very significant mass loss upon the irradiation due to the photochemical degradation of citric acid catalyzed by Fe\textsuperscript{III}(Cit). We could observe similar photocatalytic degradation for droplets containing solid Fe\textsubscript{2}O\textsubscript{3} nanoparticles and ATD inclusions. Comparing the experimentally observed mass loss of the particles containing solid inclusions with those of different concentrations of Fe\textsuperscript{III}(Cit), we conclude on the availability of iron for photocatalytic degradation: we estimate that 25% of the iron in Fe\textsubscript{2}O\textsubscript{3} nanoparticles is taking part in the photocatalytic processes but only 5−12.5% in the case of ATD. According to our PRAD model prediction of photochemical degradation in a 500 nm particle under atmospheric conditions, we conclude that while the photochemical aging processes lead to a significant particle mass loss, the photochemical processes are limited by the transport limitation of O\textsubscript{2}. For estimating the relevance of this specific photocatalytic process on organic aerosol aging on a global scale, local conditions like temperature, relative humidity, actinic fluxes, and the contents
Figure 4.3: Simulated radius change of a 500 nm particle in air with 40% RH and 293.5 K with intermittent irradiation diurnal cycle.

of iron and organic species need to be taken into account. This requires substantially extended model simulations for which the PRAD model may provide the process focused basis.
Figure 4.4: (a) Simulated average Fe(III) fraction of a particle with originally 500 nm in radius with intermittent irradiation diurnal cycle. Profiles of (b) Fe(III) fraction, (c) O$_2$ concentration, and (d) Fe(III)-Citrate concentration in the particle between the droplet center and the interface with the gas (vapor) phase.
Chapter 5

Summary and outlook

5.1 Summary

It has been demonstrated that aerosol particles can attain highly viscous, semi-solid, or even glassy states under a wide range of atmospheric conditions. The reduced mobility of aerosol constituents and low water content can limit chemical processes inside the particle. While the impact of high viscosity on dark chemical reactions has received substantial attention over the last decade (Slade and Knopf 2014; Steimer et al., 2014; Zhou et al., 2012), systematic studies on the effect of high viscosity on photochemical processes are scarce. We choose Fe\textsuperscript{III}(Cit) photolysis induced citric acid degradation as a model system to investigate the feedbacks between photochemical aging and aerosol microphysics such as diffusivity. This system was chosen since the thermodynamic properties of citric acid have been studied in detail by our group (Lienhard et al., 2012), the water diffusivity is known down to highly viscous solutions (Lienhard et al., 2014), and the viscosity has been reported recently (Marshall et al., 2016; Song et al., 2016). Furthermore, the Fe\textsuperscript{III}(Cit) complex photochemistry is well established in both solution (Abida et al., 2012; Faust and Zepp, 1993; Pozdnyakov et al., 2012) and solid states (Abrahamson et al., 1994). A kinetic model, referred to as the photochemical reaction and diffusion (PRAD) model, was developed within this project for the Fe\textsuperscript{III}(Cit)/CA photocatalytic cycle, to assess how viscosity and diffusivity influence chemical processes. The particle is divided into a number of shells, and in each shell equilibria and chemical reactions among major species are calculated. After each chemical process time step, molecules are exchanged between adjacent shells based on the respective concentration gradients and the condensed phase diffusivity of each species. There are a number of ill-constrained parameters needed in the model, such as the diffusivities of CO\textsubscript{2} and O\textsubscript{2} in citric acid solutions, the re-oxidation pathways, and their reaction constants of Fe\textsuperscript{II} to Fe\textsuperscript{III}. In order to determine some of these unknowns and to better constrain the model for the application to atmospheric conditions, dedicated experiments with single aqueous Fe\textsuperscript{III}(Cit)/citric acid particles levitated in EDB were conducted.

A conceptually simple experiment is the pulsed light exposure of particles in a N\textsubscript{2} atmosphere, which results in only one decarboxylation from the excited Fe\textsuperscript{III}(Cit) complex.
(described in Chapter 2). The production of CO$_2$ with subsequent loss to the gas phase changes particle size, mass, density, and refractive index, resulting in a shift in the Mie resonance wavelength. By an analytic treatment of resonance wavelength shifts, the diffusivity of CO$_2$ in such aqueous citric acid droplets was determined with unprecedented accuracy at different RH: for medium viscosities at intermediate RH ($\sim 25 - 40\%$ RH), $D_{\text{CO}_2} \sim 10^{-14}$ m$^{-2}$ s$^{-1}$, agreeing with the Stokes-Einstein relationship based on viscosity data reported by other groups (Marshall et al., 2016; Song et al., 2016); under very dry high-viscosity conditions, $D_{\text{CO}_2} \sim 10^{-16}$ m$^{-2}$ s$^{-1}$, which is higher than the Stokes-Einstein prediction. Meanwhile, the production and evaporation of CO$_2$ also changes the particle water activity; therefore the particles has to take up or lose water in order to keep its water activity in equilibrium with the gas phase. This transport process helped us to determine the diffusivity of water in citric acid droplets, which is 10-times higher than $D_{\text{CO}_2}$ at $\sim 25 - 40\%$ RH, but 10-times lower than $D_{\text{CO}_2}$ under dry conditions. We attribute the crossover of H$_2$O and CO$_2$ diffusivities to different molecular interactions. In highly concentrated amorphous citric acid, water molecules may encounter a local environment similar to crystalline citric acid monohydrate, which is the thermodynamically stable form. Water molecules may become more bound to the citric acid network under these circumstances, whereas the same does not occur for CO$_2$. In more dilute solutions, with more water available, CO$_2$ diffusion may be slowed down by hydrogen bonds with the water network. The CO$_2$ diffusion data will help constrain diffusivity of small molecules relevant for condensed phase chemistry in viscous SOA particles, which remained highly uncertain in the past.

The irradiation in N$_2$ not only leads to the decarboxylation of Fe$^{\text{III}}$(Cit), but at the same time reduces the photosensitive Fe$^{\text{III}}$ complex to a non-absorbing Fe$^{\text{II}}$ complex. After the irradiation, if we introduce O$_2$ to the gas phase, the following oxidative process can re-oxidize Fe$^{\text{II}}$ back to Fe$^{\text{III}}$, which then combines with another citric acid molecule to form again photochemically active Fe$^{\text{III}}$(Cit). According to how much particle mass loss is observed in a following irradiation, we could normalize that value to the mass loss of the initial irradiation, thus obtaining the Fe$^{\text{III}}$ fraction recovered in the previous O$_2$ exposure time. In Chapter 3, we measured the recovered Fe$^{\text{III}}$ fraction over O$_2$ exposure time as a function of RH. Our results show that Fe$^{\text{III}}$ recovery efficiency can reach 100% if we exposed the particle in O$_2$ for long enough time (10 h is sufficient for 48% and 65% RH). However, the recovery is slower at lower RH (at 25% RH, less than 0.4 Fe$^{\text{III}}$ is recovered even after 26 h), which is due to the diffusion limitation of O$_2$ in the particle phase. By tuning the PRAD model, we determined the diffusivity of O$_2$ in aqueous citric acid droplets: $3.2 \times 10^{-17}$ m$^2$ s$^{-1}$, $4.3 \times 10^{-15}$ m$^2$ s$^{-1}$, and $2.1 \times 10^{-13}$ m$^2$ s$^{-1}$ at 24%, 48%, and 65% RH, respectively, with the reaction rate of Fe$^{\text{II}}$(HCit) oxidized by O$_2$ directly being 0.05 M$^{-1}$ s$^{-1}$.

To test the PRAD model performance and to estimate photochemical degradation of organic particles under atmospheric conditions, we combined photoreduction and re-oxidation in experiments with irradiation for long periods (up to 2 days) in an O$_2$ atmosphere (Chapter 3). The typical experimental run was done with Fe$^{\text{III}}$(Cit)/CA (molar ratio 0.05) particles. At 293.6 K and 52% RH, the particle mass loss during irradiation in
O₂ is substantial with up to 80% of the initial mass lost to the gas phase within 24 hours. We observed an acceleration of mass loss rate. Initially it was \( \sim 2\% \, h^{-1} \), but increased to \( \sim 10\% \, h^{-1} \) after 30% to 50% mass was lost. Our model simulations reproduce this effect, providing evidence that it captures the essential chemistry and transport during irradiation. By looking into the concentration profile of each species, we propose that the production and accumulation of other low-volatile photosensitive species (such as the C₄ compound) increases the production of CO₂, thus facilitating particle mass loss. When RH decreases from 50% to 16.5% RH, the mass loss rate decreases as well. Especially in the range of 50% to 40% RH, the mass loss rate is quite sensitive to RH. According to our PRAD model, the decrease of mass loss rate with lower RH is mainly due to the transport limitation of O₂ in highly viscous particles. In that case, reactive oxygen species and free organic radicals with low diffusivity are preserved in aerosol particles, which can exacerbate the health hazards of aerosol exposure and alter atmospheric chemistry for ROS and free radical reactions previously unconsidered.

We know that mineral dust is the main source of atmospheric iron, and that most iron in the atmosphere is in the form of iron oxide (Fe₂O₃). Organic acids can promote its dissociation into soluble iron, which then participates in chemical processes in the aerosol particles. To prove this, we performed experiments of replacing Fe^{III}(Cit) with Fe₂O₃ nanoparticles (< 50 nm) and ATD dust particles (0–3 µm) as solid inclusions in aqueous citric acid droplets (Chapter 4). Both solid inclusions showed degradation of citric acid under 473 nm light, and the kinetics showed the same characteristic acceleration, even though the total mass loss was less compared to dissolved Fe^{III}(Cit). This holds in particular for the experiments with ATD, since the inclusions are large and the exact amount of available iron varied between experiments. Comparison of nominal iron with available iron in our experiments are a factor of 5 for Fe₂O₃ nanoparticles, and a factor of 8–20 for ATD particles. These Fe₂O₃ and ATD catalyzed photochemical processes confirm that even when in solid oxide form originally, dissolution of iron oxides from minerals leads to the formation of complexes in aqueous organic acid particles and facilitate the degradation of organics. In addition, we also find that non-absorbing Fe^{II}(HCit) can be oxidized by O₂ to photosensitive Fe^{III}(Cit) (see Chapter 3). Therefore, we come to the conclusion that as long as organic aerosol particles contain iron, no matter the phase or oxidation state, photochemical aging of the particles can be enhanced via iron complex photolysis initiated pathways. Finally, the PRAD model was applied to predict the photochemical aging in accumulation mode size particles with atmospheric gas phase and solar irradiation, which turns out to be limited by O₂ particle phase diffusivity, but still shows significant particle mass loss.

5.2 Outlook

The pulsed experiments in Chapter 2 enable us to derive the diffusivities of CO₂ and H₂O from the time scale of resonance wavelength shift, with the safe assumption of constant refractive index after the irradiation. However, in each experiment, at least 2 times of
irradiation were needed to make sure all Fe$^{\text{III}}$(Cit) has been photolyzed. This method can be improved by doing only one irradiation with a longer duration (such as 20 s), which will make the analysis more easy and straightforward. The same holds true for the oxygen recovery experiments discussed in Chapter 3: instead of using 500 s low intensity light, pulsed irradiation with strong intensity would save time for both measurements and data analysis. Moreover, it is also worthwhile to try with shorter wavelength (< 473 nm), where Fe$^{\text{III}}$(Cit) absorbs stronger, to even shorten the duration of pulsed irradiation and to compare the quantum yields at different wavelengths.

In the presence of O$_2$, Fe$^{\text{III}}$(Cit) photolysis triggers more radical reactions, producing various compounds with a broad range of carbon atoms. Our colleagues at PSI observed C$_3$–C$_{11}$ organic compounds in the condensed phase by HPLC-MS after several hours of UV irradiation on the Fe$^{\text{III}}$(Cit)/CA solution, and measured the kinetics of productions of HO$_2$•, acetic acid, acetaldehyde, and acetone in the gas phase by PTR-MS coupled with CWFT. Similarly, more experiments can be done to track the kinetic production of other volatile species, such as CO$_2$, which can be a direct proof of decarboxylation, and time-resolved production data can be used to tune the model. Our group is currently building a new setup coupling EDB with MS, which will enable us to identify the products in the particle phase after irradiation.

In Chapter 3, we mentioned that we did some tests with Fe$^{\text{II}}$(HCit)/CA particles as well. Fe$^{\text{II}}$(Hcit) is not photosensitive at 473 nm irradiation. However, if Fe$^{\text{II}}$(Hcit)/CA particle is levitated in the dark in an O$_2$ atmosphere for some time, Fe$^{\text{II}}$(Hcit) can be oxidized by O$_2$ directly (R10), producing Fe$^{\text{III}}$(Cit) and the HO$_2$•, which can also contribute to the oxidation of Fe$^{\text{II}}$ to Fe$^{\text{III}}$. In principle, one molecule of O$_2$ can oxidize four Fe$^{\text{II}}$ to Fe$^{\text{III}}$. While in Fe$^{\text{III}}$(Cit)/CA system, most O$_2$ may oxidize HO–•CR$_2$ to O–CR$_2$ first, since the reaction rate coefficient is more than 8 orders of magnitude faster than O$_2$ oxidizing Fe$^{\text{II}}$(Hcit) directly. In that case, one molecule of O$_2$ can only oxidize three Fe$^{\text{II}}$ to Fe$^{\text{III}}$. Therefore, it does not matter whether the aerosol particles contain Fe$^{\text{II}}$ or Fe$^{\text{III}}$. O$_2$ in the atmosphere can always transfer non-absorbing Fe$^{\text{II}}$ complex to photochemically Fe$^{\text{III}}$ complex quite efficiently. To confirm that, more tests with Fe$^{\text{II}}$(Hcit)/CA particle can be taken to evaluate O$_2$ direct oxidation efficiency at different RH.

In Chapter 3, both the re-oxidation step and the whole photochemical cycle show a strong dependence on RH, pointing out the diffusion limitation of O$_2$ in the photochemical processes. Instead of deriving the recovered Fe$^{\text{III}}$ fraction from the particle resonance wavelength shift, we observed gradients in iron oxidation states in single particles after irradiation by STXM experiments (shown in Figure 5.1), indicating a short reacto-diffusive length for O$_2$. In highly viscous atmospheric aerosol particles, the low diffusivity of O$_2$ can induce an anoxic region in the bulk, where reactive oxygen species (generated from O$_2$ present in particles prior to illumination) and free organic radicals accumulate and are preserved. If these particles are breathed in, the release of radicals and rapid formation of new ROS due to the sudden admission of O$_2$ into the humidified (and thus less viscous) particle and their release in our lung and subsequent oxidative stress can cause potential health hazards. However, it is not so straightforward to determined the diffusivity of O$_2$.
5.2. Outlook

Figure 5.1: X-ray image of spatially resolved Fe$^{III}$(Cit)/CA particle (molar ratio of 1) after 15 min of UV light irradiation at 3 W m$^{-2}$ in an atmosphere of 110 mbar of O$_2$ at 40% RH. The color scale indicates Fe$^{III}$ fraction.

in the model, since re-oxidation rates and equilibrium constants can also influence the recovery rate of Fe$^{III}$, as well as the solubility of O$_2$. We suggested to vary parameters one at a time to test the sensitivity of outcomes to each parameter.

In Chapter 4, we confirmed that iron (in Fe$_2$O$_3$ nanoparticles or ATD particles) can facilitate the photochemical aging processes of aqueous citric acid particles. While iron is widely existing in aerosol particles, either in the form of soluble or insoluble iron, its speciation and concentration is quite diverse (Deguillaume et al., 2005; Dou et al., 2015; Usher et al., 2003). It is necessary to do further experiment with atmospheric aerosol samples, to know whether and under which conditions O$_2$ transport limitation is occurring.

In addition, the PRAD model still needs to be globally optimized with the integration of the results from EDB, CWFT, and STXM simultaneously. Various experimental conditions were used: molar ratio of Fe$^{III}$(Cit)/CA, wavelength and intensity of the illumination, gas pressure of the system, and RH are all varying over a considerable range. EDB and STXM experiments were done with single particles, but with different radii (∼ 10 μm in EDB, 100–500 nm in STXM), while CWFT was done with thin films solutions. As the PRAD model does not cover all conceivable chemistry, but what is believed to be the most significant, global optimization including data of all techniques should show us, whether we are missing some essential reactions or pathways and let us constrain the highly uncertain parameters of the model even better. This will provide higher confidence when applying this model to assess aerosol aging and its influence on atmospheric partitioning as well as
on human health effects.
Appendix A

Parameters used in PRAD model
Henry's law is described as a function of temperature $T$:

$$H = H^o \cdot \exp \left( - \frac{Q}{R \cdot T} \right)$$

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$H^o$ is the Henry's law constant at 0°C and 1 atm. $Q$ is the heat of solution.

### Appendix A. Parameters used in PRAD model

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### Table A.1: Liquid phase diffusivity factors (normalized to water) and Henry's law coefficients (CH$_4$)

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<th>Diffusion coefficient $D_f$ (m$^2$/s)</th>
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Table A.2: Compilation of equilibria, chemical reactions, and corresponding rate constants in Fe\textsuperscript{III} (Cit) photochemistry system.

<table>
<thead>
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<th>number</th>
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<th>$K_{eq}/k_{\text{r}/\sigma}$</th>
<th>sources</th>
</tr>
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<td>E1</td>
<td>H\textsubscript{2}O $\rightleftharpoons$ OH\textsuperscript{−} + H\textsuperscript{+}</td>
<td>$1 \times 10^{-14}$ M</td>
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<td>E2</td>
<td>H\textsubscript{2}Cit $\rightleftharpoons$ H\textsubscript{2}Cit\textsuperscript{−} + H\textsuperscript{+}</td>
<td>$7.5 \times 10^{-4}$ M</td>
<td>Martell and Smith (1982)</td>
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<td>H\textsubscript{2}Cit\textsuperscript{−} $\rightleftharpoons$ H\textsubscript{2}Cit\textsuperscript{2−} + H\textsuperscript{+}</td>
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<td>E4</td>
<td>H\textsubscript{2}Cit\textsuperscript{2−} $\rightleftharpoons$ Cit\textsuperscript{3−} + H\textsuperscript{+}</td>
<td>$4.0 \times 10^{-7}$ M</td>
<td>Martell and Smith (1982)</td>
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<tr>
<td>E5</td>
<td>Fe\textsuperscript{3+} + Cit\textsuperscript{3−} $\rightleftharpoons$ Fe\textsuperscript{III}(Cit)</td>
<td>$1.58 \times 10^{11}$ M\textsuperscript{−1}</td>
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<td>Fe\textsuperscript{3+} + Cit\textsuperscript{3−} + H\textsubscript{2}O $\rightleftharpoons$ Fe\textsuperscript{III}(Cit)(OH)\textsuperscript{−} + H\textsuperscript{+}</td>
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<tr>
<td>E7</td>
<td>Fe\textsuperscript{3+} + H\textsubscript{2}Cit\textsuperscript{2−} $\rightleftharpoons$ Fe\textsuperscript{III}(H\textsubscript{2}Cit)\textsuperscript{+}</td>
<td>$5.0 \times 10^{6}$ M\textsuperscript{−1}</td>
<td>Martell and Smith (1982)</td>
</tr>
<tr>
<td>E8</td>
<td>Fe\textsuperscript{2+} + H\textsubscript{2}Cit\textsuperscript{2−} $\rightleftharpoons$ Fe\textsuperscript{II}(H\textsubscript{2}Cit)</td>
<td>$794$ M\textsuperscript{−1}</td>
<td>Martell and Smith (1982)</td>
</tr>
<tr>
<td>E9</td>
<td>Fe\textsuperscript{3+} + H\textsubscript{2}O $\rightleftharpoons$ Fe\textsuperscript{III}(OH)\textsuperscript{2+} + H\textsuperscript{+}</td>
<td>$6.5 \times 10^{-3}$ M</td>
<td>Smith and Martell (1976)</td>
</tr>
<tr>
<td>E10</td>
<td>O\textsubscript{2}– + H\textsuperscript{+} $\rightleftharpoons$ HO\textsubscript{2}–</td>
<td>$6.3 \times 10^{4}$ M\textsuperscript{−1}</td>
<td>Bielski et al. (1985)</td>
</tr>
<tr>
<td>E11</td>
<td>Fe\textsuperscript{2+} + O=C(CH\textsubscript{2}COO)\textsubscript{2}– $\rightleftharpoons$ Fe\textsuperscript{II}[O=C(CH\textsubscript{2}COO)\textsubscript{2}]</td>
<td>$2 \times 10^{2}$ M\textsuperscript{−1}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>E12</td>
<td>2H\textsuperscript{+} + OH\textsuperscript{−} - C(CH\textsubscript{2}COO)\textsubscript{2}– $\rightleftharpoons$ OH\textsuperscript{−} - C(CH\textsubscript{2}COOH)\textsubscript{2}</td>
<td>$3 \times 10^{2}$ M\textsuperscript{−2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>E13</td>
<td>2H\textsuperscript{+} + O=C(CH\textsubscript{2}COO)\textsubscript{2}– $\rightleftharpoons$ O=C(CH\textsubscript{2}COOH)\textsubscript{2}</td>
<td>$1.5 \times 10^{2}$ M\textsuperscript{−2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R1</td>
<td>Fe\textsuperscript{III}(Cit) + h\nu $\rightarrow$ Fe\textsuperscript{2+} + OH\textsuperscript{−} - C(CH\textsubscript{2}COO)\textsubscript{2}– + CO\textsubscript{2}</td>
<td>$1 \times 10^{-19}$ cm\textsuperscript{2}</td>
<td>Pozdnyakov et al. (2012)</td>
</tr>
<tr>
<td>R2</td>
<td>Fe\textsuperscript{III}(Cit)(OH)\textsuperscript{−} + h\nu $\rightarrow$ Fe\textsuperscript{2+} + OH\textsuperscript{−} - C(CH\textsubscript{2}COO)\textsubscript{2}– + OH\textsuperscript{−} + CO\textsubscript{2}</td>
<td>$1 \times 10^{-19}$ cm\textsuperscript{2}</td>
<td>Pozdnyakov et al. (2012)</td>
</tr>
<tr>
<td>R3</td>
<td>OH\textsuperscript{−} - C(CH\textsubscript{2}COO)\textsubscript{2}– + O\textsubscript{2} $\rightarrow$ O=C(CH\textsubscript{2}COO)\textsubscript{2}– + O\textsubscript{2}– + H\textsuperscript{+}</td>
<td>$1 \times 10^{6}$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Hug et al. (2001)</td>
</tr>
<tr>
<td>R4</td>
<td>OH\textsuperscript{−} - C(CH\textsubscript{2}COO)\textsubscript{2}– + O\textsubscript{2} $\rightarrow$ O=C(CH\textsubscript{2}COO)\textsubscript{2}– + O\textsubscript{2}– + H\textsuperscript{+}</td>
<td>$1 \times 10^{6}$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Hug et al. (2001)</td>
</tr>
<tr>
<td>R5</td>
<td>HO\textsubscript{2}– + HO\textsubscript{2}– $\rightarrow$ H\textsubscript{2}O\textsubscript{2} + O\textsubscript{2}</td>
<td>$8.3 \times 10^{5}$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Bielski et al. (1985)</td>
</tr>
<tr>
<td>R6</td>
<td>Fe\textsuperscript{2+} + O\textsubscript{2}– (−2H\textsuperscript{+}) $\rightarrow$ Fe\textsuperscript{3+} + H\textsubscript{2}O\textsubscript{2}</td>
<td>$1 \times 10^{7}$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Rush and Bielski (1985)</td>
</tr>
<tr>
<td>R7</td>
<td>Fe\textsuperscript{2+} + HO\textsubscript{2}– (+H\textsuperscript{+}) $\rightarrow$ Fe\textsuperscript{3+} + H\textsubscript{2}O\textsubscript{2}</td>
<td>$1.2 \times 10^{6}$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Rush and Bielski (1985)</td>
</tr>
<tr>
<td>R8</td>
<td>Fe\textsuperscript{2+} + H\textsubscript{2}O\textsubscript{2} $\rightarrow$ Fe\textsuperscript{3+} + *OH + OH\textsuperscript{−}</td>
<td>$76$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Walling (1975)</td>
</tr>
<tr>
<td>R9</td>
<td>Fe\textsuperscript{2+} + *OH $\rightarrow$ Fe\textsuperscript{III}(OH)\textsuperscript{2+}</td>
<td>$4.3 \times 10^{8}$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>Christensen and Schested (1981)</td>
</tr>
<tr>
<td>R10</td>
<td>Fe\textsuperscript{II}(HTct) + O\textsubscript{2} $\rightarrow$ Fe\textsuperscript{III}(Cit) + HO\textsubscript{2}–</td>
<td>$3$ M\textsuperscript{−1} s\textsuperscript{−1}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R11</td>
<td>C\textsubscript{5} + h\nu $\rightarrow$ C\textsubscript{3} + 2CO\textsubscript{2}</td>
<td>$2 \times 10^{-24}$ cm\textsuperscript{2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R12</td>
<td>C\textsubscript{4} + h\nu $\rightarrow$ C\textsubscript{3} + CO\textsubscript{2}</td>
<td>$1 \times 10^{-20}$ cm\textsuperscript{2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R13</td>
<td>C\textsubscript{5} + h\nu $\rightarrow$ C\textsubscript{2} + C\textsubscript{3}</td>
<td>$2 \times 10^{-24}$ cm\textsuperscript{2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R14</td>
<td>C\textsubscript{4} + h\nu $\rightarrow$ C\textsubscript{2} + C\textsubscript{2}</td>
<td>$1 \times 10^{-20}$ cm\textsuperscript{2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R15</td>
<td>C\textsubscript{5} + h\nu $\rightarrow$ C\textsubscript{4} + CO\textsubscript{2}</td>
<td>$2 \times 10^{-24}$ cm\textsuperscript{2}</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R16</td>
<td>C\textsubscript{5} stable fraction</td>
<td>0.5</td>
<td>tuning parameter</td>
</tr>
<tr>
<td>R17</td>
<td>radical self reaction</td>
<td>0</td>
<td>tuning parameter</td>
</tr>
</tbody>
</table>
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Overview of AMS datasets of non-refractory PM$_1$ at different types of sampling locations</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>(a) Organic aerosol aging with $\alpha$-pinene as an example. (b) Evolution of condensed-phase O:C ratio versus approximate *OH exposure during simulated aging. (c) Reactions can be classified into three categories: fragmentation, functionalization and oligomerization</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>Photocatalytic cycle of Fe$^{II}$-citrate complex in an aqueous particle containing citric acid</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Familiar substances are shown as well as their approximate dynamic viscosity at room temperature with a classification into solid, semi-solid, and liquid states. For organic liquids the molecular diffusion coefficient can be estimated from the viscosity via Eq. 1.1. The bottom panel shows the corresponding e-folding times of equilibration for various particle diameters</td>
<td>9</td>
</tr>
<tr>
<td>2.1</td>
<td>(a) Temporal evolution of Mie resonance wavelength for pulsed-light exposure experiments. (b) Zoomed-in view of irradiation #1</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>Response of the normalized mass of the particle to the first irradiation calculated from the data of Figure 2.1</td>
<td>18</td>
</tr>
<tr>
<td>2.3</td>
<td>Temporal evolution of Mie resonance wavelength, refractive index, and calculated normalized mass remaining in the particle during photochemistry at 0% RH and 293 K</td>
<td>19</td>
</tr>
<tr>
<td>2.4</td>
<td>(a) Measured and modeled particle size change with time during the drying process, left axis. Relative humidity inside EDB, right axis. (b) Residuals between simulated and measured particle sizes. (c) Simulated citric acid concentration inside the particle during the drying process. (d) Parametrization of $D_{H_2O}$ as a function of water activity</td>
<td>20</td>
</tr>
<tr>
<td>2.5</td>
<td>Diffusivities of CO$_2$ and H$_2$O as a function of water activity in Fe$^{II}$Cit/citric acid solutions</td>
<td>22</td>
</tr>
<tr>
<td>S2.1</td>
<td>An exponential decay fitting for the 10 s irradiation period at 0% RH</td>
<td>25</td>
</tr>
<tr>
<td>S2.2</td>
<td>Normalized mass ratio profile of the particle at 0% RH and 293 K</td>
<td>26</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>S2.3</td>
<td>Black crosses: raw data of observed resonance wavelength response at 0% RH before and after irradiation without correction for the residual slow water diffusion. Solid grey line: linear fit to the data prior irradiation, dashed grey line: linear fit shifted to smaller wavelength by 0.7 nm to show the steepening of resonance shift after irradiation.</td>
<td></td>
</tr>
<tr>
<td>S2.4</td>
<td>Response of normalized mass of the particle to the first irradiation (3 s duration) at 25% RH</td>
<td></td>
</tr>
<tr>
<td>S2.5</td>
<td>Photocatalytic cycle of Fe$^{III}$ (Cit) complex in an aqueous particle containing citric acid. (b) Absorption spectra of Fe$^{III}$ (Cit) (Pozdnyakov et al., 2012) (black), and the overlap with actinic flux of the sunlight at 0° zenith angle (red) (Madronich et al., 1995)</td>
<td></td>
</tr>
<tr>
<td>S2.6</td>
<td>Schematic illustration of the PRAD model</td>
<td></td>
</tr>
<tr>
<td>S2.7</td>
<td>Schematic of the experimental procedure to investigate the recovery efficiency under different relative humidities (24%, 48% and 65% RH)</td>
<td></td>
</tr>
<tr>
<td>S2.8</td>
<td>Temporal evolution of two Mie resonance wavelengths shifts normalized to the wavelength prior irradiation; blue area marks the time with irradiation (473 nm, 4 W cm$^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>S2.9</td>
<td>Fe$^{III}$ fraction after different time intervals of recovery in O$_2$</td>
<td></td>
</tr>
<tr>
<td>S2.10</td>
<td>Fe$^{III}$ (Cit)/CA (molar ratio 0.05) particle radius change with irradiation time (473 nm, 4 W cm$^{-2}$) at 300 K with different relative humidities. (b) Corresponding radius remaining from model output</td>
<td></td>
</tr>
<tr>
<td>S2.11</td>
<td>For 50% RH case, simulated (a) O$_2$, (b) HO$_2^*$, (c) CO$_2$, and (d) C$_4$ complex concentration profiles for a particle with an initial radius of 8 µm</td>
<td></td>
</tr>
<tr>
<td>S2.12</td>
<td>Typical experimental run on a Fe$^{III}$ (Cit)/citric acid (molar ratio 0.05) particle</td>
<td></td>
</tr>
<tr>
<td>S2.13</td>
<td>Photocatalytic mass loss observed under 473 nm irradiation for aqueous citric acid particles in O$_2$ at 50% RH and 293.5 K. (b) Zoomed-in view of the blue box in (a). Dotted lines are data from model simulations</td>
<td></td>
</tr>
<tr>
<td>S2.14</td>
<td>Simulated radius change of a 500 nm particle in air with 40% RH and 293.5 K with intermittent irradiation diurnal cycle</td>
<td></td>
</tr>
<tr>
<td>S2.15</td>
<td>Simulated average Fe(III) fraction of a particle with originally 500 nm in radius with intermittent irradiation diurnal cycle. Profiles of (b) Fe(III) fraction, (c) O$_2$ concentration, and (d) Fe(III)-Citrate concentration in the particle between the droplet center and the interface with the gas (vapor) phase</td>
<td></td>
</tr>
<tr>
<td>S2.16</td>
<td>X-ray image of spatially resolved Fe$^{III}$ (Cit)/CA particle (molar ratio of 1) after 15 min of UV light irradiation at 3 W m$^{-2}$ in an atmosphere of 110 mbar of O$_2$ at 40% RH</td>
<td></td>
</tr>
</tbody>
</table>
List of Tables

2.1 Summary of diffusivities of $\text{H}_2\text{O}$ and $\text{CO}_2$ at different relative humidities.  

A.1 Liquid phase diffusivity factors (normalized to water) and Henry’s law coefficients (Sander 2015) of major species in Fe$^{\text{III}}$(Cit) photochemistry system.  

A.2 Compilation of equilibria, chemical reactions, and corresponding rate constants in Fe$^{\text{III}}$(Cit) photochemistry system.  

69
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