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Cluster models for acid displacement reactions on sea salt aerosols

As we are increasingly facing the effects of global warming, studying the main climate drivers gains enormous significance. Aerosols represent one of these main climate drivers due to their ability to scatter and absorb solar radiation. They serve as cloud condensation nuclei, and they are involved in photochemical as well as chemical reactions with atmospheric trace gases [1]. Sea salt aerosols are produced from the ocean's surface and thus, the composition of young sea salt aerosols resembles that of the ocean. They contain mainly sodium chloride and water, but also a complex mixture of ions such as Mg^{2+}, Ca^{2+} or SO_4^{2-} and organic molecules [2]. During the aging process, including e.g. drying as well as chemical and photochemical reactions, the composition changes. A major chemical pathway regarding the chloride depletion in sea salt aerosols is the acid displacement reaction (see Fig. 1), which leads to the release of HCl, reaction (I):

$$NaCl_{(\text{aq or s})} + HA_{(\text{g or aq})} \longrightarrow NaA_{(\text{aq or s})} + HCl_{(\text{g or aq})} \tag{I}$$

where HA is an acidic species such as sulfuric acid (H_2SO_4), nitric acid (HNO_3) or an organic acid, and A is the corresponding conjugate base of HA [1,3]. This reaction has first been observed for sulfuric and nitric acid on sea salt aerosols in the atmosphere [4, 5] and on the surface of NaCl crystals in laboratories [6-8]. Somewhat surprisingly, also weaker organic acids like formic and pyruvic acid contribute significantly to chloride depletion *via* acid displacement, reaction (I) [2, 3].

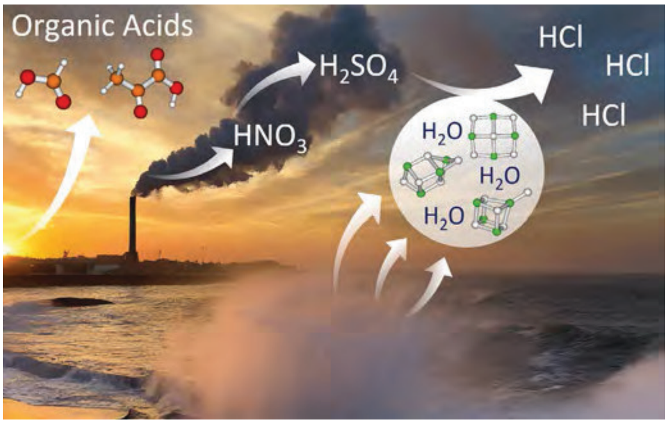

Fig. 1: HCl is released by the acid displacement reaction (I) on sea salt aerosols in our atmosphere.

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Experiment

In our laboratory, we develop cluster models for reactions of sea salt aerosols in our atmosphere, such as the acid displacement reaction (I). We perform reactivity experiments of cationic and anionic NaCl clusters (see Fig. 2a) in the gas phase under ultra-high-vacuum (UHV) conditions ($\approx 10^{-10}$ mbar) on a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The gas-phase sodium chloride cluster ions are produced *via* electrospray ionization using isotopically enriched $Na^{35}Cl$. The reaction gas (HA) is introduced via a leak valve into the ICR cell, where the reaction itself takes place, increasing the UHV pressure to $\approx 10^{-8}$ mbar. Reaction kinetics are recorded by taking mass spectra after exposing the cluster ions to the reaction gas in the ICR cell for variable time. As reaction gas (HA) the organic acids pyruvic acid, formic acid, acetic acid and acetonitrile are used. The reactants are chosen to cover a wide range of proton affinities of their conjugate bases (A), ranging from 1395 kJ/mol to 1561 kJ/mol [9].

Acid displacement reaction

The reaction kinetics yield a sequential uptake of the reaction gas (HA) by anionic as well as cationic NaCl clusters with HCl release according to the acid displacement reaction (I). Fig. 2b illustrates this sequential reaction for the cationic cluster $[Na_6Cl_5]^+$ with formic acid (HCOOH). Each uptake of HCOOH leads to a proton transfer from the acid to a Cl^- ion in the NaCl cluster, forming HCl. The formiate ion $HCOO^-$ then replaces the chloride in the cluster and HCl is released. The overall sequential reaction observed in our experiments, for cations and anions, respectively, can be described via reactions (II) and (III):

$$[Na_xCl_x]Na^+ + yHA \longrightarrow [Na_xCl_{x\text{-}y}(A)_y]Na^+ + yHCl \tag{II}$$

$$[Na_xCl_x]Cl^- + yHA \longrightarrow [Na_xCl_{x\text{-}y}(A)_y]Cl^- + yHCl \tag{III}$$

Here x describes the cluster size and y the number of consecutive reactions. Since our reactivity experiments are performed in the gas phase under UHV conditions, we can demonstrate that the acid displacement reaction (I) takes place between the pristine NaCl cluster ions and the reaction gas HA in the absence of water or any other substance that might promote the reaction.

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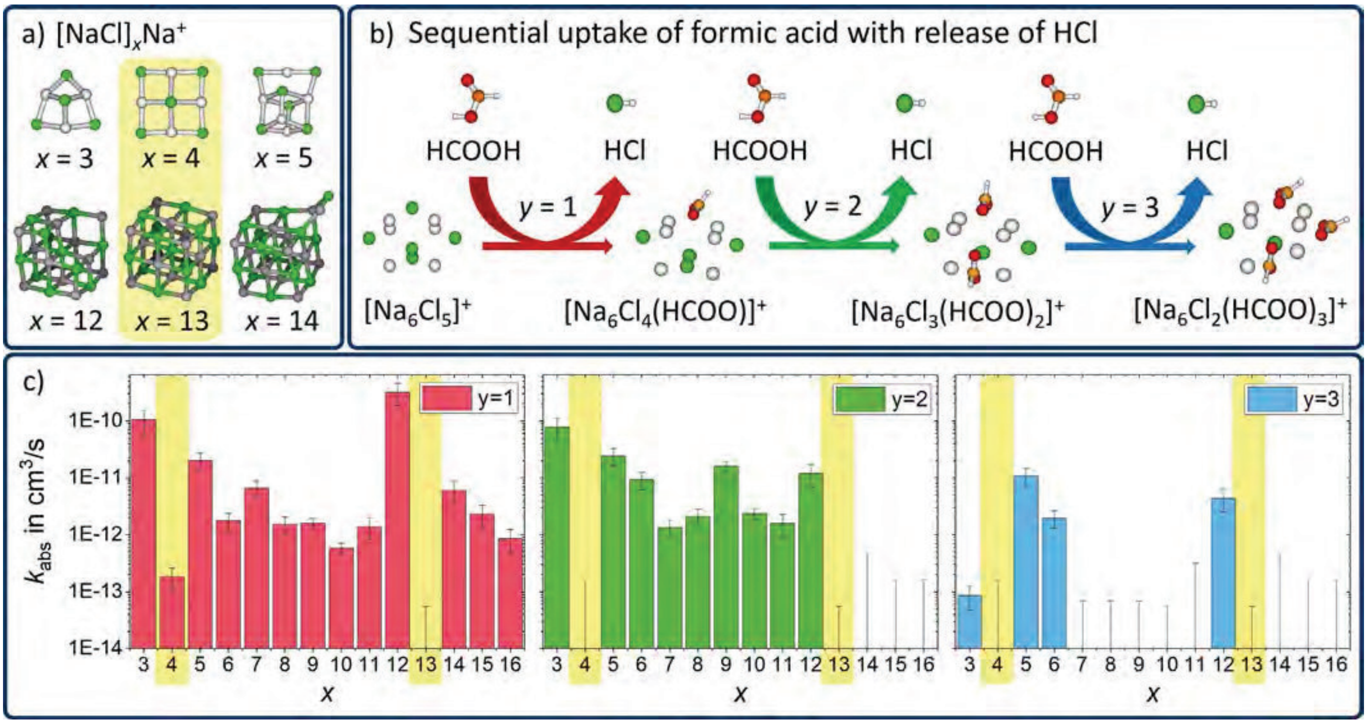

Fig. 2: a) Structures of the cationic clusters $[NaCl]_xNa^+$ for x = 3, 4, 5 and x = 12, 13, 14. b) Sequential acid displacement reaction (II) for the cationic cluster $[Na_6Cl_5]^+$ with the reaction gas formic acid (HCOOH). c) The absolute rate coefficients k_{abs} for the reactions of the cationic NaCl clusters $[NaCl]_xNa^+$ with formic acid as a function of the cluster size x according to reaction (II). The cluster sizes only plotted with an error bar did not react and the error bar marks the upper limit of the reaction rate coefficient, estimated from the noise level of the corresponding reaction kinetics. In a) and c), magic cluster sizes [10] are highlighted in yellow.

Comparing the reaction kinetics of different reaction gases (HA) yields a correlation between reactivity and the proton affinity of the acid's conjugate base (A). This can be well explained by the fact that the relevant reaction step within the acid displacement reaction is the proton transfer from the acid to a Cl^- in the NaCl cluster, forming HCl. Thus, in our studies, the highest reactivity is observed for pyruvic acid ($CH_3COCOOH$), with the lowest proton affinity of the conjugate base. Furthermore, the maximum number y_{max} of consecutive reaction steps observed within a limited time correlates with proton affinity, where no reaction is observed with acetonitrile, one step with acetic acid, three steps for formic acid, and complete displacement of all chloride ions for pyruvic acid. Hence, the maximum number y_{max} of sequential displacement reactions increases with increasing acidity. The absolute rate coefficients k_{abs} depend significantly on the cluster size x and vary over several orders of magnitude, as illustrated in Fig. 2c for the reaction gas formic acid. If one compares the rate coefficients for a specific cluster size x, the value is highest for pyruvic acid, one or two orders of magnitude lower for formic acid, and again one or two orders of magnitude lower for acetic acid.

Magic cluster sizes

The absolute rate coefficients k_{abs} for the reactions of the cationic NaCl clusters with formic acid as a function of the cluster size x are plotted in Fig. 2c for cluster sizes up to x = 16 and reactions up to y_{max} = 3. The absolute rate coefficients k_{abs} for different cluster sizes x vary over several orders of magnitude. The magic cluster sizes x = 4 and x = 13, identified in previous studies [10], show reduced reactivity. These highly symmetric cluster sizes (see Fig. 2a) are characterized by a high stability and a low reactivity and thus have high intensities in mass spectra. In contrast, their neighbouring cluster sizes have defects causing a low stability and a high reactivity. We recently explained the magic character of the smallest magic cluster x = 4 by statistical modelling of the complete phase space of the cluster sizes x = 3, 4, 5 [11]. While the magic anion $[NaCl]_4Cl^-$ is thermochemically favored, the high abundance of the cationic $[NaCl]_4Na^+$ is explained by the inherently slow loss of an atomic fragment, an entirely entropic effect. For the small magic cluster x = 4, acid displacement y = 1 is one to three orders of magnitude slower than for non-magic cluster sizes. For the large magic cluster x = 13, which is a cubic section of the NaCl fcc lattice, no reaction at all could be observed. In contrast, the direct neighbors of the magic cluster sizes exhibit the highest absolute rate coefficients and contribute three of the four cluster sizes that show the third reaction step with formic acid within 20 s reaction time.

Conclusion

Our reactivity experiments yield a sequential uptake of the reaction gas (HA) by anionic as well as cationic NaCl clusters with release of HCl, mirroring the acid displacement reaction (I) found in aerosol studies [1, 3]. The results indicate that the reactivity of sea salt aerosols in the troposphere [4, 5] (see Fig. 1) and reactions on the surface of NaCl crystals in laboratories [6-8] does not necessarily rely on the presence of water. We show that reactivity towards a specific acid (HA) anticorrelates with the proton affinity of its conjugate base (A), *i.e.*, the higher the proton affinity, the slower the reactions. Additionally, we found a significantly reduced reactivity for the magic cluster sizes x = 4 and x = 13 and a strikingly high reactivity for the neighbouring cluster sizes. This strongly suggests that defects promote the acid displacement reaction.

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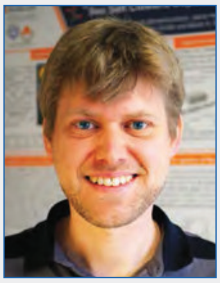
Jessica Hartmann studied physics at the University of Innsbruck, Austria. She worked as a student assistant in the chemical physics group of Martin Beyer between 2019 and 2022, doing mass spectrometry, spectroscopy and quantum chemical calculations. In 2022, she started her PhD in the same group, focusing on salt clusters.



PD Dr. Christian van der Linde

Christian van der Linde received his Diploma in Chemistry in 2009 and his PhD in Physical Chemistry in 2012 from Kiel University, Germany. After graduation, he worked 2013–2014 as a postdoc in the group of James M. Lisy at the University of Illinois at Urbana-Champaign, USA, on IRMPD of small alkalimetal based clusters. Since 2015, he works as postdoc, and since 2019 as senior scientist at the University of Innsbruck, Austria, in the group of Martin Beyer, combining mass spectrometry and spectroscopy methods to study ion chemistry, spectroscopy and photochemistry of various cluster systems. In 2024, he obtained his habilitation at the University of Innsbruck.

Prof. Dr. Martin K. Beyer

Martin Beyer studied physics and got a PhD in physical chemistry at TU Munich in 1999. After staying at UC Berkeley with a Feodor Lynen postdoctoral fellowship of the Alexander von Humboldt foundation, he went back to TU Munich for his habilitation. He received the Heinz Maier Leibnitz Award 2003, jointly given by DFG and BMBF, and obtained the *venia legendi* at TU Munich in 2004. In 2005, Martin Beyer moved to TU Berlin as a DFG Heisenberg Fellow. He held a professor position for physical chemistry at Kiel University before moving to the University of Innsbruck, where he heads the chemical physics group at the Institut für Ionenphysik und Angewandte Physik. His research focuses on chemistry, spectroscopy and photochemistry of molecular ions and ionic clusters, chemical ionization methods for gas analysis, and fundamental concepts in mechanochemistry.

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