The Fluorite-Water Interface upon Flow: A Vibrational Sum Frequency Generation Spectroscopy Study

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Statutory Declaration

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In chapters 4 to 7, I will write in the first person plural instead of singular (we instead of I) to make the text more readable and to account for the specified contributions of others to those chapters.

Patrick Ober

Outline and Own Contribution

This thesis covers the investigation of flow-induced changes in chemical equilibria at the fluorite-water interface by using interface-specific vibrational Sum Frequency Generation (v-SFG) spectroscopy. Chapter 1 gives a brief introduction to the research topic, and Chapter 2 explains the concepts to understand the conducted research. The experiments and methods used are described in Chapter 3. The subsequent Chapters 4 to 7 cover the results and scientific discussion, and Chapter 8 provides a brief outlook.

Chapter 4 characterizes the impact of flow on concentration profiles and the surface charge along the fluorite-water interface. The study provides insights into the coupling of the dissolution and surface charging process via the fluoride concentration with fluoride adsorption/desorption determining the surface charge and thus the v-SFG intensity. This collaborative study is part of an article published in the journal *Nature Communications*.

In Chapter 5, the combination of flow experiments and v-SFG spectroscopy is used to uncover calcium adsorption/desorption as an additional process contributing to the surface charging at the fluorite-water interface. This second process is quantified to be several orders of magnitude smaller than fluoride adsorption/desorption. Consequently, flow experiments combined with v-SFG spectroscopy constitute a highly sensitive approach to study the interplay between interfacial reactions.

By applying the introduced approach to the fluorite-water interface with different ions added to the aqueous phase, chapter 6 studies ion-specific effects. The found interactions include charge screening and adsorption.

Finally, Chapter 7 provides a perspective on the dynamics that arise when the flow velocity is changed. Those dynamics cover the temporal development of velocity and concentration profiles and their connection to the surface charge, quantified through the v-SFG intensity. An important finding is an initial turbulence arising at high flow rates.

Chapters 4 to 7 are collaborative studies connected to a publication or manuscript in preparation. The individual author contributions are summarized on the next page. I contributed to those studies in the design of the research project, the data analysis, discussion, and interpretation, and as (co-)lead author in writing the manuscripts. Furthermore, I performed the spectroscopic experiments, partly assisted by Sophia Henriette Kolbinger. The model used in chapter 4, which was developed for his simulations by Willem Q. Boon, was extended by me to capture the second adsorption/desorption process within Chapter 5.

Parts of this thesis are based on the following publications

- Ober, P., Boon, W. Q., Dijkstra, M., Backus, E.H.G., van Roij, R., & Bonn, M. Liquid flow reversibly creates a macroscopic surface charge gradient. *Nature Communications*, *12*, 4102 (2021). © The Authors 2021
- 2. Ober, P., Hunger, J., Kolbinger, S.H., Backus, E.H.G., & Bonn, M. Flow experiments reveal the interplay of different adsorption reactions at a mineral-water interface. (in preparation)
- Ober, P., Kolbinger, S.H., Backus, E.H.G., & Bonn, M. Studying ion-specific interactions at a mineral-water interface by surface-specific spectroscopy and flow experiments. (in preparation)
- 4. Ober, P., Backus, E.H.G., & Bonn, M. Studying non-equilibrium conditions at a mineral-water interface by surface-specific spectroscopy. (in preparation)

Throughout the whole thesis, there are paragraphs and figures that are taken or modified from the above-mentioned publications and manuscripts, including their supporting information. The co-authors and journals gave me their permission for the reproduction. The author contributions to those publications are specified as follows:

- 1. P.O., E.H.G.B., and M.B. designed the experimental part of the research project and provided a qualitative interpretation of the experimental results. P.O. performed the experiments and analyzed the data. W.Q.B., M.D., and R.v.R. provided a quantitative interpretation of the experimental results. W.Q.B. performed the numerical and analytic calculations and generalized the findings. All authors discussed the results and wrote the manuscript. P.O. and W.Q.B. contributed equally.
- 2. P.O., J.H., E.H.G.B., and M.B. designed the research project. P.O. and S.H.K. performed the experiments, P.O. analyzed the data and developed the modelling. All authors discussed the results and wrote the manuscript.
- 3. P.O., E.H.G.B., and M.B. designed the research project. P.O. and S.H.K. performed the experiments, P.O. analyzed the data. All authors discussed the results and wrote the manuscript.
- 4. P.O., E.H.G.B., and M.B. designed the research project. P.O. performed the experiments and analyzed the data. All authors discussed the results and wrote the manuscript.

Further publications:

- Ober, P., Rogg, S., & Hess, C. Direct Evidence for Active Support Participation in Oxide Catalysis: Multiple Operando Spectroscopy of VOx/Ceria. *ACS Catalysis*, **10**, 2999 (2020).
- Haroun, F., El Haitami, A., Ober, P., Backus, E. H. G., & Cantin, S. Poly (ethylene glycol)block-poly (propylene glycol)-block-poly (ethylene glycol) Copolymer 2D Single Network at the Air–Water Interface. *Langmuir*, *36*, 9142 (2020).

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Abstract

The present thesis studies spectroscopically flow-induced changes in chemical equilibria at the fluorite-water interface.

Vibrational Sum Frequency Generation (v-SFG) spectroscopy is used to probe the net orientation and polarization of interfacial water molecules and thus measures the surface charge of fluorite. A few years ago, similar experiments demonstrated that flow increases the positive surface charge of fluorite under acidic conditions [LIS et al., *Science* 2014]. This surface charging was explained by enhanced desorption of fluoride anions due to the dilution upon flow.

By studying the changes upon flow along the mineral's surface, a flow-induced surface charge gradient is found. This gradient correlates with a gradient in fluoride concentration. Supported by numerical simulations, it is shown that coupling of charge-neutral dissolution with the fluoride adsorption/desorption reaction explains those gradients. In further experiments, the fluoride dilution upon flow is systematically suppressed, revealing the small contribution of calcium adsorption/desorption to the surface charge. Additionally, the interaction of the fluorite surface with other ions in aqueous solutions is investigated. Such interactions include charge screening and adsorption. Finally, the dynamics upon changing the flow rate are addressed. The observed non-linear behavior points to turbulences prior to the formation of a laminar flow profile.

Zusammenfassung

Die vorliegende Doktorarbeit behandelt die spektroskopische Untersuchung strömungsinduzierter Verschiebungen chemischer Gleichgewichte an der Fluorit-Wasser Grenzfläche.

Vibrational Sum Frequency Generation (v-SFG, Schwingungssummenfrequenzgenerierungs-) Spektroskopie fragt die Nettoorientierung und Polarisierung von Wassermolekülen an der Grenzfläche ab und wird somit zur Bestimmung der Fluorit-Oberflächenladung genutzt. Vor wenigen Jahren konnte mit ähnlichen Experimenten gezeigt werden, dass Strömungen die positive Oberflächenladung von Fluorit in Kontakt mit sauren Lösungen erhöht [LIS et al., Science 2014]. Eine verstärkte Desorption von Fluoridanionen aufgrund einer strömungsbedingten Konzentrationsverringerung diente als Erklärung dieser Ladungsänderung.

Die Untersuchung der strömungsinduzierten Änderungen entlang der Mineraloberfläche zeigt einen Gradienten in der Oberflächenladung unter Strömungsbedingungen. Dieser Gradient geht mit einem Konzentrationsgradienten der Fluoridanionen einher. Unterstützt durch numerische Simulationen wird gezeigt, dass eine Kopplung ladungsneutraler Mineralauflösung und der Adsorption/Desorption von Fluoridanionen derartige Gradienten erklärt. In weiteren Experimenten mit systematisch abnehmendem Verdünnungseffekt wird der geringe Beitrag der Adsorption/Desorption von Calciumkationen zur Oberflächenladung aufgedeckt. Auch die Wechselwirkungen der Fluoritoberfläche mit anderen Ionen in wässriger Lösung wird thematisiert. Diese Wechselwirkungen beinhalten die Abschirmung der Oberflächenladung und Adsorptionsreaktionen. Abschließend wird ein Ausblick zur Dynamik bei einer Änderung der Flussgeschwindigkeit gegeben. Das zu beobachtende nichtlineare Verhalten deutet auf Turbulenzen während der Ausbildung eines laminaren Flussprofils hin.

1 Introduction

"God made the bulk; surfaces were invented by the Devil" is a famous quote of the renowned physicist Wolfgang Pauli. His statement addresses the special nature of a material's surface. While the bulk represents a continuum of similar atoms or molecules, the environment of an atom or molecule at the surface changes abruptly.¹ This sudden break gives rise to unique properties and has implications on the chemical behavior. In fact, surface reactions play an important role in geochemistry, biochemistry, electrochemistry, and heterogeneous catalysis.¹⁻⁶

Solid surfaces are often in contact with a flowing fluid. One prominent example is the mineral-water interface, where the processes occur, which determine mineral growth and dissolution as well as environmental remediation.^{2,3} Mineral-water interfaces can gain additional complexity when they are charged, as the electric field affects the structure of the aqueous phase. To enable geochemical and geophysical modelling and sensing, it is crucial to understand the interplay between chemical reactions, the surface charge, and the structure of interfacial water molecules as well as ion distributions.⁷⁻¹⁰ However, it can be very challenging to obtain such a molecular insight as it becomes evident from the common mineral fluorite (or calcium fluoride, CaF₂). In fact, there have already been several studies on the fluorite-water interface.¹⁰⁻²¹ Despite those research efforts many open questions remain, particularly regarding the surface chemistry of this mineral. For instance, the coupling of surface charge and dissolution or the interaction with ions that this mineral could face in contact with aqueous solutions appears worth investigating.

Once again, one can quote Wolfgang Pauli when aiming for a molecular understanding of an interface, because it is challenging to study the small surface compared to the gigantic bulk.^{22,23} Thus, one needs a method that is sensitive to the interface. In terms of non-invasive spectroscopic methods, there are certain non-linear techniques, which by selection rule are interface-specific and therefore provide tools to study the interface of interest. At aqueous interfaces, vibrational Sum Frequency Generation (v-SFG) spectroscopy is a well-established method that is not only interface-specific but also provides molecular specificity due to the resonance of infrared (IR) radiation and molecular vibrations. Therefore, v-SFG can provide information on interfacial molecules, for instance, their orientation.^{10,15,21,23-34} The presence of an electric field arising from a charged surface aligns the dipole moments of the interfacial water molecules and polarizes the water molecules some nanometers into the solution. Both phenomena increase the magnitude of the observed v-SFG signal. Therefore, the v-SFG response can be used as a measure of the electric field at the surface. ^{8,10,21,23,25-40}

³

In natural settings, the mineral is often in contact with an aqueous phase that is not only moving but also changes its flow behavior (e.g. the flow rate and the stream profiles) depending on external conditions. Nevertheless, most v-SFG studies of mineral-water interfaces have not directly addressed the role of flow or have even investigated static conditions only. In 2014 LIS et al.¹⁰ showed that chemical equilibria of mineral surfaces (including fluorite) in contact with water can be altered when the aqueous phase is in motion. They observed a flow-induced change in the v-SFG intensity reporting a reversible change in surface charge upon flow. The explanation was a flow-induced change in the local concentration of the dissolved ions, which affects the adsorption/desorption of these ions and thus the surface charge. While the impact of applied flow on the surface chemistry is already an essential finding, this study also paved the way for SCHAEFER et al.³³, who used flow-induced dilution to quantify interfacial concentrations due to dissolution and thereby studied the kinetics of silica dissolution.

The present thesis builds up on the mentioned v-SFG studies at mineral-water interfaces upon flow and investigates the surface chemistry of fluorite further. First, the flow-induced alteration of fluorite's surface charge will be studied on a macroscopic scale, which provides an insight into the surface charge distribution upon flow as well as the coupling of the dissolution reaction and the surface charge. Afterwards, the molecular picture of the coupling will be extended by unravelling the interplay of different adsorption/desorption reactions. Moreover, the interaction of the surface with different ions will be studied by the flow-induced changes in the surface charge tracked by the v-SFG intensity. Finally, there will be an outlook on the dynamics upon changing the flow rate.

2 Theoretical Background

This chapter aims to provide an overview of the concepts needed to understand the scientific questions addressed in the present thesis. It covers the concept of adsorption/desorption, the structure of the aqueous phase at charged interfaces, the mathematical description of fluid flow and mass transport, as well as the basics of the spectroscopic method used. Parts of section 2.4 have been published in the Supporting information of the publication "Liquid flow reversibly creates a macroscopic surface charge gradient", *Nature Communications* **12**, 4102 (2021). Particularly the sections 2.4.1 and 2.4.5 are modified and extended versions of this previous work.

2.1 Adsorption/Desorption Reactions

At a mineral-water interface, a wide variety of chemical reactions can take place. One example that plays a key role in the present work is the adsorption of a particle, which can generally be described by the reaction in equation (2.1). Here S represents the surface, A the adsorbing particle or adsorbate, and SA the adsorbed state or occupied surface site. The adsorption reaction is usually reversible, which means that the particle can also be released. This reverse reaction is called desorption.⁴¹

$$S + A \rightleftharpoons SA$$
 (2.1)

The simplest description of adsorption/desorption processes was introduced in 1916 by Irving Langmuir based on his experiments on solid-gas interfaces.⁴² The underlying assumptions of his model are:

- 1. Adsorption does not exceed a monolayer since the attractive forces between the surface and the first layer are much stronger than those between the first layer and outer layers.
- 2. There is a finite number of equivalent surface sites, where adsorption occurs.
- 3. Adsorbed molecules do not interact with each other.^{41,42}

Based on these assumptions and the reaction in equation (2.1), the time derivative of the number of occupied surface sites Γ_{SA} is given in equation (2.2), which is simply the difference between the adsorption and the desorption rate.^{41,43}

$$\frac{d\Gamma_{\rm SA}}{dt} = k_{\rm ads} \cdot \Gamma_{\rm S} \cdot c_{\rm A} - k_{\rm des} \cdot \Gamma_{\rm SA} \tag{2.2}$$

Here, the adsorption process is determined by the rate constant k_{ads} , the number of unoccupied surface sites Γ_S and the concentration of the adsorbate c_A . Similarly, the desorption process is described by the rate constant k_{des} and the number of occupied surface sites Γ_{SA} . Since the Langmuir model assumes a finite number of equivalent surface sites, the sum of Γ_{SA} and Γ_S is a constant value $\Gamma = \Gamma_{SA} + \Gamma_S$. One can also relate these numbers of sites to the surface area leading to a density. Often, neither a number of sites nor a density is used but a surface coverage.^{41,43}

To characterize the adsorption process, the number of occupied surface sites Γ_{SA} is of interest. This value is accessible from the model for the equilibrated system. In equilibrium, the rate of adsorption equals that of desorption, and the number of occupied surface sites remains constant. In this case, equation (2.2) equals zero, and can therefore be solve for Γ_{SA} , leading to the Langmuir isotherm in equation (2.3).⁴¹

$$\Gamma_{\rm SA} = \frac{\Gamma \cdot c_{\rm A}}{c_{\rm A} + k_{\rm des}/k_{\rm ads}}$$
(2.3)

Based on this equation, some possible scenarios can be discussed. If there is no adsorbate present ($c_A = 0$) the surface site occupancy is zero. For low concentrations, the denominator in equation (2.3) is approximately constant, and thus the number of occupied surface sites is proportional to the concentration. Finally, for very high concentrations, every surface site is occupied, leading to a monolayer.⁴²

The assumptions of the Langmuir model make it simple. This simplicity, however, let it fail to describe more realistic systems, since their description require a higher degree of complexity. For instance, the limitation to a monolayer is one aspect, which was challenged by later studies and addressed in 1938 by a multilayer-model of Stephen Brunauer, Paul Emmet, and Edward Teller, which is nowadays called BET-isotherm.^{41,44} Moreover, models have been established that also take interactions of the occupied sites into account, where the adsorption becomes less likely with increasing coverage of the surface. One example is the Freundlich isotherm named after Herbert Freundlich.^{41,45}

2.2 Electrical Double Layer

The chemistry at the mineral-water interface is connected to local concentrations and the surface charge of the mineral. Therefore, it is crucial to have a molecular picture of the interface. The surface charge of a mineral may depend on conditions as the pH but also on the mineral itself. Mechanisms generating the surface charge of the mineral can be protonation/deprotonation in the case of oxides as silica and sapphire or ion exchange between the mineral and the solution in the case of ionic crystals.^{7,10,15,46} Due to electrostatic interactions, the presence of a surface charge changes the structure of the aqueous solution close to the surface compared to the bulk solution, e.g. orientation and polarization of water molecules as well as ion distributions. This special interfacial structure is called the Electrical Double Laver (EDL). A schematic illustration is shown in Fig. 2.1. The concept of the EDL is thereby not limited to mineral surfaces but is also used to describe other natural or technical settings where an aqueous solution is in contact with a charged surface. This could be, for instance, a biological system like a cell membrane or an electrochemical setting with an electrode.^{7,10,36,47}

Over time, several models were developed to describe the EDL. The attraction of counterions towards the charged surface was first treated as a parallel plate capacitor by Hermann von Helmholtz. In his model, the capacitor consists of the charged surface and the first layer of attracted counterions. The center of the counter ions is referred to as the Outer Helmholtz Plane (OHP). Both, the OHP and the charged surface form the so-called Helmholtz or Stern layer. Within this layer, the potential decreases linearly, as shown in Fig. 2.1 in the near-surface region.^{7,48-50}

Another model was proposed by Louis Georges Gouy and David Leonard Chapman, which is a mean-field description for the charged surface in contact with an aqueous phase using the following assumptions:

- 1. The surface is sharp, and the charge is homogenously distributed.
- 2. Ions are point charges, and only electrical forces (Coulomb interactions) are present.
- 3. Water is a homogenous dielectric continuum.⁷

Based on these assumptions, the Poisson equation (2.4) for the position dependency of the potential $\Phi(x)$ can be solved with a Maxwell-Boltzmann distribution of the ions as shown in equation (2.5).^{7,50-52}



Fig. 2.1. Illustration of the electrical double layer. At a positively charged surface, the first layer of water molecules are oriented with the oxygen towards the surface. Additionally, counter ions (anions) are attracted. This first layer of water molecules and the counterions forms the so-called Stern layer. The center of the ions is also referred to as the Outer Helmholtz Plane (OHP). Between the charged surface and the OHP, the potential decreases linearly from the surface potential Φ_0 . In the diffuse layer, the potential decreases like an exponential. Similarly, the organization of the water molecules and ions transits towards a bulk-like distribution where no more influence of the charged surface is present.

$$\frac{d^2\Phi(x)}{dx^2} = -\frac{4\cdot\pi\cdot\sigma_{\rm V}}{\epsilon_0\cdot\epsilon_{\rm r}} \quad \text{with} \quad \sigma_{\rm V} = \sum_i z_i \cdot e \cdot N_{\rm A} \cdot c_i(x) \tag{2.4}$$

$$c_i(x) = c_{i,b} \cdot \exp\left(-\frac{z_i \cdot e \cdot \Phi(x)}{k_{\rm B} \cdot T}\right)$$
(2.5)

In these two equations, σ_V is the charge density that depends on the ion's valence z_i , the elementary charge e, and the number of ions i per volume or the local concentration c_i times the Avogadro constant N_A . The index b denotes the bulk concentration as a value for a homogenous distribution far away from the charged surface or at infinite temperature. Further, ϵ_0 is the electric permittivity of vacuum and ϵ_r the relative permittivity of the present medium (e.g. water), T is the temperature and k_B is the Boltzmann constant. This distribution of ions is called the diffuse layer and leads to an exponential-like decay of the potential into the solution, as shown in Fig. 2.1 on the right side of the OHP.

For a flat surface with a low surface potential ($\Phi_0 < 25 \text{ mV}$), one can derive an expression that connects the surface charge density σ with the surface potential Φ_0 (equation (2.6)), where I_c is the ionic strength as a charge-weighted concentration of ions in the solution.^{53,54}

$$\Phi_{0} = \frac{2 \cdot k_{\rm B} \cdot T}{\rm e} \operatorname{asinh}\left(\frac{\sigma}{\sqrt{8 \cdot k_{\rm B} \cdot T \cdot N_{\rm A} \cdot I_{\rm c} \cdot \epsilon_{0} \cdot \epsilon_{\rm r}}}\right) \quad \text{with} \quad I_{\rm c} = \frac{1}{2} \cdot \sum_{i} z_{i}^{2} \cdot c_{i,\rm b} \tag{2.6}$$

At low potentials, equation (2.5) can also be linearized as done within the approximation of Peter Debye and Erich Hückel. This leads to an exponential decay of the potential. A characteristic length describing this decay is the Debye screening length λ_D from equation (2.7). This length decreases with concentration and is ~1nm under physiological conditions but can also reach the µm scale at neutral pH and low electrolyte concentrations.^{7,41,50,55}

$$\lambda_{\rm D} = \sqrt{\frac{\epsilon_0 \cdot \epsilon_{\rm r} \cdot k_{\rm B} \cdot T}{I_{\rm c} \cdot N_{\rm A} \cdot e^2}} \tag{2.7}$$

Despite the agreement of both the Gouy-Chapman model and the Debye-Hückel theory with several experimental studies, one can question the underlying assumptions. The neglect of the finite ion size and the presence of an ion's hydration shell was addressed by Otto Stern. In his theory, he combined the models of the Helmholtz layer and the diffuse layer. Herein, the potential drops linear within the first layer of adsorbed ions and decays rather exponentially in the following diffuse layer, as shown in Fig. 2.1.^{7,50,56}

Over the years, several shortcomings of the above-mentioned models were reported, and extensions were made to yield more accurate descriptions.^{7,54,57-59} For instance, David Caldwell Grahame included the adsorption of counterions without hydration shell to the charged surface. Thereby, he introduced the Inner Helmholtz Plane (IHP) at the center of the adsorbed counterions. In this model, IHP and OHP together form the Stern layer.^{7,54,57}

2.2.1 Electrokinetic Phenomena

Experiments to determine the electric state of a surface typically rely on electrokinetic phenomena. Whenever shear between a charged surface and the adjacent fluid is present, such electrokinetic phenomena arise. The characteristic value here is the zeta potential Φ_{ζ} . Due to the large electrostatic forces closer to the charged surface, there are layers of water molecules and ions that are rather rigid and do not move. The plane where the transition between this rigid environment and the moving fluid occurs, defines the plane of shear. As introduced above, the potential decreases from the charged surface into the solution. The potential at the plane of shear is the zeta potential Φ_{ζ} , which is usually close to the OHP.^{54,60}

The relation between shear and potential can be used to get an insight into the electrical state of the interface. A common experiment is electrophoresis, where a potential gradient is applied to

a solution containing large charged particles, such as colloids. Due to the external electric field, movement of the particles is observed. A velocity can be determined and related to the potential.^{54,61} However, to study charged solid surfaces streaming potential measurements are the method of choice. There, fluid flow is applied, introducing shear in the diffuse layer, leading to an induced potential along the flow channel. This so-called streaming potential Φ_{stream} is connected to the zeta potential according to equation (2.8) via the pressure drop Δp , the dynamic viscosity η , and the electrical conductivity κ of the aqueous phase.^{61,62}

$$\Phi_{\text{stream}} = \frac{\Phi_{\zeta} \cdot \epsilon_0 \cdot \epsilon_r \cdot \Delta p}{4 \cdot \pi \cdot \eta \cdot \kappa}$$
(2.8)

2.3 Fluid Dynamics

The previous sections gave an insight into concepts that can be applied to the mineral-water interface on a rather microscopic scale. With the introduction of macroscopic movement of the aqueous phase (i.e., flow), also a rather macroscopic dimension needs to be included in the treatment of the system under investigation.

2.3.1 From the Navier-Stokes to Bernoulli's and Stream Profiles

The most important equation for the mathematical treatment of fluid dynamics dates back to the 19th century. Based on Newton's conservation of momentum, Claude Louis Marie Henri Navier and George Gabriel Stokes described the velocity field of a fluid in space and time. Their conclusions are expressed in the Navier-Stokes equation (2.9).

$$\frac{d\boldsymbol{u}}{dt} = -\boldsymbol{u} \cdot di\boldsymbol{v}(\boldsymbol{u}) + \boldsymbol{a} - \frac{1}{\rho} \cdot grad(p) + \frac{\eta}{\rho} \cdot grad(di\boldsymbol{v}(\boldsymbol{u}))$$
(2.9)

Here u is the velocity, t the time, a the acceleration, ρ the density, p the pressure, η the dynamic viscosity. The left-hand side of the equation gives the temporal change in the velocity field, while the first term on the right-hand side gives its spatial change. Additionally, the terms on the right-hand side of the equation take into account the accelerating forces like gravitation, applied pressure, and friction. The only simplifying assumptions the Navier-Stokes equation relies on, are the homogeneity and the incompressibility of the medium. Still, one needs powerful simulation software to solve the Navier-Stokes equation for the investigated system.^{43,63,64}

Despite the complexity of the Navier-Stokes equation, it is possible to simplify the equation with reasonable assumptions to gain insights into some phenomena. For instance, when neglecting friction, equation (2.9) simplifies into Euler's equation. In one dimension and under static conditions (du/dt = 0) Euler's equation can be integrated into Bernoulli's equation (2.10), which is a textbook example used to describe why an airplane can fly.^{43,63,65}

$$p_{\text{tot}} = p + \rho \cdot g \cdot H + \frac{1}{2}\rho \cdot u^2 = const.$$
(2.10)

Here, p_{tot} is the total pressure, g is the gravitational acceleration of the earth, and H is the height.

Another important insight is the Poiseuille stream profile in a pipe with impermeable walls. For fully developed flow $(d\mathbf{u}/dt = 0 \text{ and } du_i/di = 0$, where *i* is a coordinate) without radial and swirl components $(\mathbf{u} = u_z)$ and upon neglecting gravity, a pressure drop Δp along a pipe of the length *L* and radius *R* can be related to friction at the pipe wall only. With the boundary condition of zero tangential velocity at the pipe's wall (no-slip), one obtains a radial stream profile, as shown on the left of Fig. 2.2. Its mathematical description is the parabolic Poiseuille profile with the velocity as a function of the radial coordinate *r* as in equation (2.11). The maximum velocity is in the center of the pipe at r = 0.43,66



Fig. 2.2. Illustration of stream profiles in a pipe (cross-section). A fluid (colored area) flows through a pipe with the radius R (grey lines at $r = \pm R$ denote the pipe's wall) in the direction of the black arrows inside the fluid. Along the pipe in the flow direction, there is a pressure drop as indicated by the brightness of the liquid. The arrows inside the fluid represent streamlines. The length of the arrows indicates the velocity of the individual streamline. The blue curves represent the velocities of all streamlines. For laminar flow (the two profiles on the left), the velocity changes parabolically with the maximum velocity in the center of the pipe (r = 0). The fluid moves only in one direction (z). The one profile on the right shows the stream profile for turbulent flow at high flow rates, where the fluid moves chaotically with velocity components not only in the z-direction. For the two laminar profiles, the distinction between the no-slip (left) and slip (middle) boundary conditions is shown. Within the no-slip boundary condition, the velocity of the fluid is zero at the wall of the pipe, while it is different from zero within the slip boundary condition. A measure for the slip velocity is the slip length L_{slip} , which is an extrapolation of the profile to zero velocity.

$$u_z(r) = \frac{\Delta p \cdot R^2}{4 \cdot \eta \cdot L} \cdot \left(1 - \frac{r^2}{R^2}\right) = u_{z,\max} \cdot \left(1 - \frac{r^2}{R^2}\right)$$
(2.11)

2.3.2 Slip and No-slip Boundary Condition

The Poiseuille profile relies on the no-slip boundary ($u_z(R) = 0$) condition, which is well established. When this boundary condition was introduced in the 19th century, it was also experimentally justified by Charles Augustin de Coulomb. He found that the resistance of an oscillating metallic plate was hardly changing when varying its surface by covering it with sandstone. Since then, there have been several controversies about that boundary condition. Even George Gabriel Stokes considered slipping ($u_z(R) > 0$) at some point but rejected it later. Also, Claude Louis Marie Henri Navier initially took slipping into account that would scale with the shear.^{67,68} Despite the lack of a compelling argument for the no-slip boundary condition, it had been consistent with a variety of non-miniaturized studies.⁶⁹ However, around the turn of the last millennium, new experimental insights have challenged the no-slip boundary condition.⁷⁰ The slip boundary conditions was reintroduced and characterized by the slip length L_{slip} , which is an extrapolation of the wall position to zero velocity (see middle of Fig. 2.2 and equation (2.12)). It was found that the slip length and thus the contribution of slip increases with the hydrophobicity of the surface as well as the shear rate.⁷⁰⁻⁷³ In contrast, with a rough and/or hydrophilic surface, a no-slip description works better.⁷⁴⁻⁷⁶

$$u(r=R) = L_{\rm slip} \cdot \frac{du}{dr}$$
(2.12)

With the augmented interest in confined geometries, where the ratio between the area of the solid surface and the fluid volume becomes rather high, the contribution of slip to the flow increases.^{76,77} Therefore, the investigation, particularly the simulation, of the flow behavior near the channel wall remains an important scientific objective.⁷⁸

2.3.3 Turbulences and the Reynolds Number

The Poiseuille profile additionally relies on the neglect of velocity elements orthogonal to the pipe direction, as radial and swirl velocities. Clearly, the fluid is not a continuous medium but consists of atoms and molecules, leading to velocity elements in the radial and swirl direction due to diffusion. More importantly, however, turbulences can arise. For high flow rates, it has been observed that the movement of a fluid reaches a state where it is not linear anymore but

chaotic, as illustrated in the right part of Fig. 2.2. The formation of such turbulences can be favored when the fluid path contains hindrances like a rough surface.^{63,64,79}

A quantitative characterization of the transition from laminar to turbulent flow is possible through the Reynolds number *Re*, named after Osborne Reynolds, who first observed turbulences in transparent pipes by using colored liquids.⁷⁹ The Reynolds number is a dimensionless quantity that reports on the ratio of inertial to viscous forces. The formula to calculate the Reynolds number depends on the geometry of the flow channel. For a circular pipe with diameter d_p , the Reynolds number is given by equation (2.13). For other geometries, the diameter d_p can usually be replaced by a hydraulic diameter, which is the ratio of the crosssectional area and the length of the participating periphery. For a circular pipe, the transition from laminar to turbulent flow occurs typically at Reynolds numbers above 2300. This value also varies with the geometry of the flow system.^{43,63,80}

$$Re = \frac{u \cdot \rho \cdot d_{\rm p}}{\eta} \tag{2.13}$$

2.3.4 Mass Transport

Advection, which is motion by stream, is not the only possibility for mass transport, since there are additional processes like diffusion. The whole complexity of mass transport can be seen in the describing differential equation (2.14). Going from left to right, the terms on the right-hand side of the equation account for advection, diffusion, chemical reactions, and mass transfer.^{43,81}

$$\frac{dc_i}{dt} = -\operatorname{div}(c_i \cdot \boldsymbol{u}) + D_i \cdot \operatorname{div}(\operatorname{grad}(c_i)) + v_i \cdot r_c \pm \beta_i \cdot a_s \cdot \Delta c_i$$
(2.14)

Here, c_i is the concentration of a component *i* at a given position and time, D_i is the diffusion coefficient, v_i is the stoichiometric number for a chemical reaction, r_c the reaction rate, β_i the mass transfer coefficient, a_s the exchange area, and Δc_i the difference in concentration between both sides of an interface. Due to the first term in equation (2.14), the mass transport in a flow system is coupled to the velocity profile of the fluid and thus to the Navier-Stokes equation (2.9). This provides the basis for the mathematical description of a system where a chemical reaction is coupled to the presence of flow, which is one objective of this thesis.

Similar to the Reynolds number as a measure for the streaming behavior, there are also index numbers characterizing mass transport. The Péclet number *Pe* (after Jean Claude Eugène Péclet) relates mass transport via convection to mass transport via diffusion (equation (2.15)).

The Sherwood number *Sh* (after Thomas Kilgore Sherwood) relates mass transfer to diffusion according as in equation (2.16).^{43,82}

$$Pe = \frac{u \cdot L}{D}$$
(2.15)

$$Sh = \frac{\beta \cdot L}{D}$$
(2.16)

2.4 V-SFG Spectroscopy

Molecular insights into mineral-water interfaces under static and flow conditions can be obtained by non-linear spectroscopy.^{10,33,83} Particularly, vibrational Sum Frequency Generation (v-SFG) spectroscopy is a well-established approach and, therefore, used within this work. The following section outlines the method's conventional background and its suitability for the targeted system.

2.4.1 Basic Concept

Within the dipole approximation, incident light induces a dipole moment μ , which on a macroscopic scale (i.e., averaging over many molecules), is the polarization P. For weak incident fields, the induced dipole moment or polarization scales linearly with the electric field via the polarizability α and the susceptibility $\chi^{(1)}$, respectively. However, suppose the electric field E is strong, as for laser pulses, higher-order (non-linear) terms need to be taken into account as in equations (2.17) and (2.18) for the dipole moment and the polarization, respectively. The proportionality between dipole moment and electric field for the higher-order contributions are the first- and second-order hyperpolarizability β and γ , respectively. For the polarization the proportionality contains the second- and third-order nonlinear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$.²⁴

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \boldsymbol{\alpha} \cdot \boldsymbol{E} + \boldsymbol{\beta} \cdot \boldsymbol{E}^2 + \boldsymbol{\gamma} \cdot \boldsymbol{E}^3 + \cdots$$
(2.17)

$$\boldsymbol{P} = \boldsymbol{P}^{(1)} + \boldsymbol{P}^{(2)} + \boldsymbol{P}^{(3)} + \dots = \epsilon_0 \cdot \left(\chi^{(1)} \cdot \boldsymbol{E} + \chi^{(2)} \cdot \boldsymbol{E}^2 + \chi^{(3)} \cdot \boldsymbol{E}^3 + \dots \right)$$
(2.18)

In SFG spectroscopy, two laser pulses overlap in space and time at the interface of interest. The total electric field at the interface is given by the sum of the electric fields of the two incident laser pulses according to (2.19), where ω is the angular frequency and by convention $\omega_1 > \omega_2$.²⁴

$$\boldsymbol{E} = \boldsymbol{E}_1 \cdot \cos(\omega_1 \cdot t) + \boldsymbol{E}_2 \cdot \cos(\omega_2 \cdot t)$$
(2.19)

From combining equations (2.18) and (2.19), several contributions to $P^{(2)}$ arise as shown in equation (2.20). Those contributions contain the double of the incident frequencies, the sum of the two frequencies or their difference. The mixing of frequencies is referred to as Sum Frequency Generation (SFG) and Difference Frequency Generation (DFG). The frequency doubling occurs individually and does not require the presence of the second electric field. The frequency doubling process is known as Second Harmonic Generation (SHG) and can be considered as a particular case of SFG ($\omega_1 = \omega_2$).²⁴

$$P^{(2)} = \epsilon_{0} \cdot \chi^{(2)} \cdot (E_{1}^{2} \cdot \cos^{2}(\omega_{1} \cdot t) + E_{2}^{2} \cdot \cos^{2}(\omega_{2} \cdot t) + E_{1} \cdot E_{2} \cdot \cos(\omega_{1} \cdot t) \cdot \cos(\omega_{2} \cdot t)) = \epsilon_{0} \cdot \chi^{(2)} \cdot \left(\frac{1}{2} \cdot E_{1}^{2} \cdot (1 + \cos(2 \cdot \omega_{1} \cdot t)) + \frac{1}{2} \cdot E_{2}^{2} \cdot (1 + \cos(2 \cdot \omega_{2} \cdot t)) + \frac{1}{2} \cdot E_{1} \cdot E_{2} \cdot \left(\cos((\omega_{1} + \omega_{2}) \cdot t) + \cos((\omega_{1} - \omega_{2}) \cdot t))\right)$$
(2.20)

Within this thesis, only the SFG process is of interest. Therefore, the discussion continues with the SFG component of the second-order non-linear polarization within the convention that the time dependency is not explicitly stated (equation (2.21)).

$$\boldsymbol{P}_{\text{SFG}}^{(2)} = \boldsymbol{\epsilon}_0 \cdot \boldsymbol{\chi}^{(2)} \cdot \boldsymbol{E}_1 \cdot \boldsymbol{E}_2 \tag{2.21}$$

2.4.2 Interfacial and Molecular Specificity

Second-order optical processes like SFG are inherently interface specific. This specificity can be illustrated by a spectrum of the fluorite-water interface at pH 14, as shown in Fig. 2.3. Two broad bands appear at ~3200 and ~3400 cm⁻¹, which can be assigned to the OH-stretch vibration of water molecules close to a negatively charged surface like calcium fluoride at high pH.^{25,84} The broadness of those bands arises from the diverse hydrogen-bonding environment of the water molecules that affect the strength of the intramolecular OH-bond. In contrast, the band at ~3650 cm⁻¹ is comparably sharp. This band can be assigned to the hydroxide species attached to the calcium fluoride surface at high pH. The shift to higher frequencies as well as the sharpness of the band, are due to minimal interactions between this surface hydroxide group and water molecules from the aqueous phase.^{10,15,18} Since this band at ~3650 cm⁻¹ arises from a surface species, the prominence of the band in the shown spectrum emphasizes the high sensitivity of the spectroscopic method towards the interface.



Fig. 2.3. V-SFG Spectrum of the fluorite-water interface at pH 14. V-SFG spectrum in the OH-stretch region of the fluorite-water interface at pH 14 (NaOH). To obtain this $|\chi_{yyz}^{(2)}|^2$ spectrum, the spectrum measured in ssp polarization combination was normalized to the shape of the IR pulse by a reference spectrum of a gold-coated fluorite prism. Additionally, the spectral shape was corrected for the frequency dependency of the Fresnel coefficients at the fluorite-water and the fluorite-gold interface. Details of the polarization combination, the normalization, and the Fresnel correction follow in sections 2.4.3 and 2.4.4, respectively.

The reason for the interfacial specificity of second-order optical processes is the non-linear susceptibility $\chi^{(2)}$. This second-order susceptibility is a third rank tensor with 27 elements because it connects every direction of the polarization with every direction of the electric fields. Therefore, equation (2.21) could also be written as equation (2.22). For instance, $P_{x,SFG}$ can be created from $E_{y,1}$ and $E_{z,2}$ with $\chi^{(2)}_{xyz}$ or $P_{z,SFG}$ can be created from $E_{z,1}$ and $E_{z,2}$ with $\chi^{(2)}_{xyz}$. The order of indices of $\chi^{(2)}_{ijk}$ corresponds to SFG (*i*), radiation 1 (*j*), and radiation 2 (*k*) with decreasing frequencies.²⁴

$$\boldsymbol{P}_{\text{SFG}}^{(2)} = \sum_{i}^{x,y,z} \boldsymbol{P}_{i,\text{SFG}}^{(2)} = \epsilon_0 \cdot \sum_{i}^{x,y,z} \sum_{j}^{x,y,z} \sum_{k}^{x,y,z} \chi_{ijk}^{(2)} \cdot \boldsymbol{E}_{j,1} \cdot \boldsymbol{E}_{k,2}$$
(2.22)

In a centrosymmetric environment like bulk water, all directions are equivalent: $\chi_{ijk}^{(2)} = \chi_{-i-j-k}^{(2)}$. However, for a third rank tensor, a change in the sign of the three subscripts is the same as reversing the axis system. Consequently, the direction of the physical phenomena described by $\chi_{ijk}^{(2)}$ is also reversed in sign: $\chi_{ijk}^{(2)} = -\chi_{-i-j-k}^{(2)}$. It is only possible to meet both conditions when $\chi_{ijk}^{(2)} = 0$. Therefore, a centrosymmetric medium does not contribute to $P_{SFG}^{(2)}$. In contrast, at an interface where symmetry is broken, $\chi_{i,j,k}^{(2)}$ can be different from zero and thereby contribute to $P_{SFG}^{(2)}$.²⁴

Another remark regarding symmetry is that an isotropic planar surface has a C_{∞} rotation axis. If the surface has its normal in *z* direction, *x* and *y* can be interchanged, and only the following components contribute: $\chi_{zzz}^{(2)}, \chi_{zxx}^{(2)} (= \chi_{zyy}^{(2)}), \chi_{xzx}^{(2)} (= \chi_{yzy}^{(2)}), \chi_{xxz}^{(2)} (= \chi_{yyz}^{(2)})$. In other words: Apart from zzz, only terms that are quadratic in *x* (or *y*) contribute.²⁴

Usually, one uses a visible (Vis) and an infrared (IR) laser pulse for SFG measurements. By detecting the SFG intensity as a function of the IR frequency, molecular specificity is obtained because a vibrational spectrum of the interface is measured. The term vibrational Sum Frequency Generation (v-SFG) spectroscopy accounts for this specificity. Still, the frequency of the obtained spectrum is shifted to the visible range of light, which is an experimental advantage as the detection is easiest in that range of light.²⁴

The molecular property behind $\chi^{(2)}$ is the second-order hyperpolarizability β . While the axis system used so far with x, y, z is based on the macroscopic surface, the molecular coordinate system does usually not coincide with the macroscopic coordinate system. The relation between the coordinate systems can be described by three Euler angles $\psi_{\rm E}$, $\phi_{\rm E}$, $\theta_{\rm E}$. The rotation matrices $R(\psi_{\rm E})$, $R(\phi_{\rm E})$, and $R(\theta_{\rm E})$ enable the conversion between the coordinate systems. Like $\chi^{(2)}_{ijk}$, the second-order hyperpolarizability $\beta_{\alpha\beta\gamma}$ is a third rank tensor with 27 elements but refers to the molecular coordinate system, which is indicated by the different indices. On the molecular level, $\beta_{\alpha\beta\gamma}$ can be derived from quantum mechanics, as shown in equation (2.23), where ω_{ν} denotes the frequency of a resonance, and τ is the relaxation time of the excited vibrational state.²⁴

$$\beta_{\alpha\beta\gamma} = \frac{\pi}{h} \cdot \frac{M_{\alpha\beta} \cdot A_{\gamma}}{(\omega_{\nu} - \omega_{IR} - i \cdot \tau^{-1})}$$
(2.23)

Here, *h* is the Planck constant while $M_{\alpha\beta}$ and A_{γ} represent the Raman and IR transition dipole moment. To be SFG active, a vibration must thus be both Raman and IR active.²⁴

The conversion from $\beta_{\alpha\beta\gamma}$ to $\chi_{ijk}^{(2)}$ involves summation over all illuminated molecules and takes into account the orientation of the molecules by the rotation matrices as shown in equation (2.24). The magnitude of $\chi_{ijk}^{(2)}$ does therefore depend on the number of molecules per volume *N* as well as their net-orientation.^{24,85}

$$\chi_{ijk}^{(2)} = \frac{N}{\epsilon_0} \sum_{\alpha\beta\gamma} \langle R(\psi_{\rm E}) R(\phi_{\rm E}) R(\theta_{\rm E}) \beta_{\alpha\beta\gamma} \rangle$$
(2.24)

So far, only a resonant contribution was considered. However, it should be mentioned that there can also be non-resonant contributions, for instance, if molecules are adsorbed on a substrate and the substrate is SFG active but not in resonance with the radiation. In such a case $\chi^{(2)}$ can be written as a sum of a resonant and a non-resonant contribution. Nevertheless, the resonant contribution is usually larger than the non-resonant one, particularly in the case of dielectric media.²⁴

2.4.3 Polarization Combinations

It is clear from equation (2.22) that many components of $\chi^{(2)}$ can be involved in the generation of SFG polarization, particularly if the electric field contains components in different directions. In order to probe specific elements of $\chi^{(2)}$ the components of the electric fields of the incident laser pulses can be limited by using linear polarized light. The two basic linear polarizations are s and p. As shown in Fig. 2.4, the electric field vector of s-polarized light points in y-direction while the one of p-polarized light lies in the x-z-plane and has thus components of x- and z-directions. The precise x- and z-contribution depend on the angle of incidence θ as described in equation (2.25). The polarizations of the incident laser pulses determine the polarization of the generated SFG radiation. A list of possible combinations for an isotropic surface and which elements of $\chi^{(2)}$ are probed is given in Table 2.1.²⁴

$$\boldsymbol{E} = \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} = \begin{pmatrix} E_p \cdot \cos(\theta) \\ E_s \\ E_p \cdot \sin(\theta) \end{pmatrix}$$
(2.25)



Fig. 2.4. Illustration of polarized E fields at the interface. The electric fields of incident radiation relative to the interface are illustrated for s- and p-polarized light. The big arrow represents the incident beam with the incident angle θ relative to the surface normal. The interface (blue area) lies in the x-y-plane with the surface normal (dashed line) in the z-direction. The plane of incidence is composed in z- and x-directions. The electric field vector of s-polarized light points in the y-direction (left) while the one of p-polarized light lies in the plane of incidence (right). The sketch is made based on Figure 2 of reference [24].

Table 2.1 Probing $\chi^{(2)}$ elements with polarization combinations. List of possible polarization combinations for an isotropic surface and which elements of $\chi^{(2)}$ are probed. The polarization combinations are in the order of decreasing frequencies (SFG, Vis, IR).²⁴

Polarization combination	Elements of $\chi^{(2)}$
pss	$\chi^{(2)}_{zyy}$
sps	$\chi^{(2)}_{yzy}$
ssp	$\chi^{(2)}_{yyz}$
ррр	$\chi^{(2)}_{ZZZ}, \chi^{(2)}_{ZXX}, \chi^{(2)}_{XZX}, \chi^{(2)}_{XZX}$

2.4.4 Local Field Correction and Normalization

At the interface, not only the electric fields of the incident radiation are present but also those of the reflected radiation. This total local field depends on the geometry and the refractive indices of the two media in contact. The consideration of geometry and refractivity is expressed by Fresnel factors.^{24,86} Thus, the effective second-order non-linear susceptibility $\chi_{eff}^{(2)}$, that is probed in a certain polarization combination, contains the elements according to Table 2.1 as well as the Fresnel coefficients or local field coefficients L_{ii} as in the equations (2.26) to (2.29). Fig. 2.5 illustrates the geometry of the beam path with the incident angle θ , the refracted angle $\gamma_{\rm r}$, and the refractive indices n_i of medium i.^{24,86}

$$\chi_{\text{eff,ssp}}^{(2)} = L_{yy}(\omega_{\text{SFG}}) \cdot L_{yy}(\omega_{\text{vis}}) \cdot L_{zz}(\omega_{\text{IR}}) \cdot \sin(\theta_{\text{IR}}) \cdot \chi_{yyz}^{(2)}$$
(2.26)

$$\chi_{\text{eff,sps}}^{(2)} = L_{yy}(\omega_{\text{SFG}}) \cdot L_{zz}(\omega_{\text{vis}}) \cdot L_{yy}(\omega_{\text{IR}}) \cdot \sin(\theta_{\text{Vis}}) \cdot \chi_{yzy}^{(2)}$$
(2.27)

$$\chi_{\text{eff,pss}}^{(2)} = L_{zz}(\omega_{\text{SFG}}) \cdot L_{yy}(\omega_{\text{vis}}) \cdot L_{yy}(\omega_{\text{IR}}) \cdot \sin(\theta_{\text{SFG}}) \cdot \chi_{zyy}^{(2)}$$
(2.28)

$$\chi_{\text{eff,ppp}}^{(2)} = -L_{xx}(\omega_{\text{SFG}}) \cdot L_{xx}(\omega_{\text{vis}}) \cdot L_{zz}(\omega_{\text{IR}}) \cdot \cos(\theta_{\text{SFG}}) \cdot \cos(\theta_{\text{Vis}}) \cdot \sin(\theta_{\text{IR}}) \cdot \chi_{xxz}^{(2)}$$

$$-L_{xx}(\omega_{\text{SFG}}) \cdot L_{zz}(\omega_{\text{vis}}) \cdot L_{xx}(\omega_{\text{IR}}) \cdot \cos(\theta_{\text{SFG}}) \cdot \sin(\theta_{\text{Vis}}) \cdot \cos(\theta_{\text{IR}}) \cdot \chi_{xzx}^{(2)}$$

$$+L_{zz}(\omega_{\text{SFG}}) \cdot L_{xx}(\omega_{\text{vis}}) \cdot L_{xx}(\omega_{\text{IR}}) \cdot \sin(\theta_{\text{SFG}}) \cdot \cos(\theta_{\text{Vis}}) \cdot \cos(\theta_{\text{IR}}) \cdot \chi_{zxx}^{(2)}$$

$$+L_{zz}(\omega_{\text{SFG}}) \cdot L_{zz}(\omega_{\text{vis}}) \cdot L_{zz}(\omega_{\text{IR}}) \cdot \sin(\theta_{\text{SFG}}) \cdot \sin(\theta_{\text{Vis}}) \cdot \sin(\theta_{\text{IR}}) \cdot \chi_{zzz}^{(2)}$$

$$(2.29)$$



Fig. 2.5. Beam path at the interface. At the interface between two media (grey and blue area) an incident beam (green arrow) can transmit in the second medium or be reflected. The transition into the second medium involves an alteration of the angle to the surface normal (dashed line) from θ to γ_{r} . This process is called refraction and is determined by the refractive indices of the two media n_1 and n_2 .

The Fresnel coefficients L_{ii} are given in the equations (2.30) to (2.32). The angle between the surface normal and the SFG radiation can be calculated from the incident angles of Vis and IR and the phase-matching condition from equation (2.33) in reflection geometry. The refracted angle can be calculated by Snell's law from equation (2.34) and n' is the refractive index of the interfacial layer.^{24,87-89}

$$L_{xx}(\omega) = \frac{2 \cdot n_1(\omega) \cdot \cos(\gamma_r)}{n_1(\omega) \cdot \cos(\gamma_r) + n_2(\omega) \cdot \cos(\theta)}$$
(2.30)

$$L_{yy}(\omega) = \frac{2 \cdot n_1(\omega) \cdot \cos(\theta)}{n_1(\omega) \cdot \cos(\theta) + n_2(\omega) \cdot \cos(\gamma_r)}$$
(2.31)

$$L_{ZZ}(\omega) = \frac{2 \cdot n_2(\omega) \cdot \cos(\theta)}{n_1(\omega) \cdot \cos(\gamma_r) + n_2(\omega) \cdot \cos(\theta)} \cdot \left(\frac{n_1(\omega)}{n'(\omega)}\right)^2$$
(2.32)

$$n_1(\omega_{\rm SFG}) \cdot \omega_{\rm SFG} \cdot \sin(\theta_{\rm SFG}) = n_1(\omega_{\rm Vis}) \cdot \omega_{\rm Vis} \cdot \sin(\theta_{\rm Vis}) + n_1(\omega_{\rm IR}) \cdot \omega_{\rm IR} \cdot \sin(\theta_{\rm IR})$$
(2.33)

$$n_1(\omega) \cdot \sin(\theta) = n_2(\omega) \cdot \sin(\gamma_r) \tag{2.34}$$

The refractivity of the interfacial layer n' introduced in equation (2.32) is controversially discussed in the literature. Depending on the conditions, it appears appropriate to use the refractive index of one out of the two media or a mixing of the indices, for which different models exist.⁸⁷⁻⁹²

The introduced Fresnel factors are crucial for extracting the $\chi^{(2)}$ spectrum from the effective one. When calculating the Fresnel coefficients, only those of the IR will influence the spectral shape, because the visible pulse has a narrow frequency band and there is little dispersion in the SFG frequency range.⁸⁷ The intensity that is measured in the end can therefore be described by the proportionality illustrated in equation (2.35) for ssp polarization combination as an example. Since the intensity *I* scales with the square of the electric field and for the generated radiation, the electric field scales with the induced polarization, only the square of $\chi^{(2)}$ is directly accessible.

$$I_{\text{SFG,ssp,Sample}}(\omega_{IR}) \sim \left|\chi_{\text{yyz,Sample}}^{(2)}(\omega_{IR})\right|^{2} \cdot \left|L_{zz,\text{Sample}}(\omega_{IR})\right|^{2} \cdot I_{\text{Vis}} \cdot I_{\text{IR}}(\omega_{IR})$$
(2.35)

Another aspect that needs to be taken into account when considering the measured spectrum is that a broadband femtosecond IR pulse was used in this work. This IR pulse covers a certain frequency range at every shot. At the detector, the generated v-SFG pulses accumulate in intensity over time. As the spectral shape of the IR pulse is not uniform, the measured spectrum needs to be normalized to the IR shape in order to extract the $|\chi^{(2)}|^2$ spectrum of the probed interface. Therefore, it is necessary to divide the measured intensity of the sample by that of a reference. For measurements at a mineral-water interface, one can use the non-resonant spectrum of a gold-coated mineral. While $\chi^{(2)}$ of the reference can be assumed constant due to its non-resonant nature, the Fresnel coefficient of the reference interface could still change over the IR range and must therefore be considered.^{25,93} Equation (2.36) is used for the exemplary conversion from the measured intensity spectra to the $|\chi^{(2)}_{yyz,Sample}|^2$ spectrum.

$$\left|\chi_{yyz,\text{Sample}}^{(2)}(\omega_{IR})\right|^{2} \sim \frac{\left|L_{zz,\text{Reference}}(\omega_{IR})\right|^{2}}{\left|L_{zz,\text{Sample}}(\omega_{IR})\right|^{2}} \cdot \frac{I_{\text{SFG,Sample}}(\omega_{IR})}{I_{\text{SFG,Reference}}(\omega_{IR})}$$
(2.36)

To illustrate the conversion from the measured spectrum in ssp polarization combination to the $|\chi_{yyz}^{(2)}|^2$ spectrum, Fig. 2.6 shows raw spectra at the gold-coated fluorite prism (a) as reference for the IR shape, the fluorite-water interface at pH 3 (b), the ratio between the calculated Fresnel coefficients of sample and reference (c), and the extracted $|\chi_{yyz}^{(2)}|^2$ spectrum (d). One can note that the ratio of the Fresnel coefficients in Fig. 2.6c is of particular importance as it varies dramatically over the investigated frequency range. This is connected to the usage of total internal reflection geometry, which is employed to enhance the signal.⁸⁶ The final $|\chi_{yyz}^{(2)}|^2$ spectrum compares well with spectra from literature.¹⁸ At the positively charged fluorite interface at acidic pH, the spectrum in the OH-stretch region is dominated by the band at ~3200 cm⁻¹, which can be assigned to water molecules that experience strong hydrogen bonding.¹⁹



Fig. 2.6. Illustration of spectra correction for ssp polarization combination. (a) Background-subtracted spectrum of a gold-coated fluorite prism as reference for spectral shape of the IR pulse. **(b)** Background-subtracted spectrum of the fluorite-water interface at pH 3, which are the standard conditions for experiments within this work. **(c)** Ratio between the squared Fresnel coefficients of the fluorite-water and fluorite-gold interface for an incident IR angle of 76°. **(d)** $|\chi_{yyz}^{(2)}|^2$ spectrum of the fluorite-water interface at pH 3. To obtain this spectrum, two corrections are necessary. First, the raw spectrum of the fluorite-water interface at pH 3 was normalized to the raw spectrum of the fluorite-gold interface, which accounts for the shape of the IR pulse. Second, this normalized spectrum was corrected for the frequency dependency of the Fresnel coefficients by dividing the normalized spectrum by the ratio from (c).

2.4.5 Probing Charged Mineral-Water Interfaces

SHG and v-SFG spectroscopy have been employed intensively to investigate charged mineral-water interfaces. Particularly the magnitude of the measured signal can be used as a measure for the surface charge and the arising surface potential. This relationship can be used, for instance, to study the adsorption of ions, the buildup in concentration due to dissolution, or to determine the point of zero charge, which is the pH of the aqueous phase where the mineral in contact with is uncharged. All those spectroscopic studies gives important insights into the surface chemistry at a mineral-water interface.^{10,19,26,29,33,38,94-97}

To discuss the connection of surface charge and the v-SFG response, one can come back to the simple proportionality of the observed intensity and $\chi^{(2)}$ as in equation (2.37).

$$I_{\rm SFG} \sim \left|\chi^{(2)}\right|^2 \cdot I_{\rm Vis} \cdot I_{\rm IR} \tag{2.37}$$

In section 2.4.2, the importance of symmetry breaking was discussed in order to make $\chi^{(2)}$ non-zero. The connection of symmetry and $\chi^{(2)}$ being zero can also be understood as a canceling of the individual molecular hyperpolarizabilities. Thus, a net orientation of the interfacial molecules is also crucial because, in the case of a random orientation of interfacial molecules, individual contributions again cancel out. For the mineral-water interface, a net-orientation of interfacial water molecules results from the presence of a surface charge due to electrostatic interactions of the water molecules' dipole moments with the electric field of the charged surface.^{10,24,89,96}

The presence of the additional electric field arising from the surface charge not only aligns water molecules but also generates polarization into the solution, which is an additional break in symmetry, resulting in an additional contribution to the v-SFG intensity. Since this contribution is connected to the interaction with the additional electric field a $\chi^{(3)}$ -term needs to be added to equation (2.37). According to GONELLA et al.³⁵, this is done by multiplying an effective third-order susceptibility $\chi^{(3)}$, with the integral of the static electric field (E_{DC} with DC = direct current) into the solution as in equation (2.38).^{25,35,96,98}

$$I_{\rm SFG} \sim \left| \chi^{(2)} + \chi^{(3)'} \cdot \int_0^\infty E_{\rm DC}(z) \, dz \right|^2 \cdot I_{\rm vis} \cdot I_{\rm IR}$$
(2.38)

The decay of the electric field into the solution and the dependency on the ionic strength has already been described in section 2.2. To take this decay into account for the v-SFG intensities, the Gouy-Chapman model can be applied.^{25,35}

The experiments for this thesis were performed in total internal reflection geometry. Under these conditions, no light is transmitted in the second medium, which enhances the observed signal by orders of magnitude.⁸⁶ Still, an evanescent field is generated at the interface and penetrates into the solution. Since this field decays exponentially with the distance from the interface, the probing depth is limited.⁹⁹ There is a complex interplay between the probing depth and the Debye depth as a measure for the depth the electric field from the charged surfaces polarizes into the solution.^{25,35,96,99,100} If the penetration depth were shorter than the Debye length, the penetration depth would determine to which extent the $\chi^{(3)}$ -term contributes to the signal. However, for the ionic strength within this thesis (mM concentration range) the penetration depth of the evanescent field is much larger than the Debye length. Thus, the decay of the evanescent field can be neglected. Within this limit, the integral from equation (2.38) results only in the surface potential Φ_0 .^{25,35} As described by GONELLA et al.³⁵, a large Debye length in the range of μ m can lead to destructive interference of the generated radiation. Thus, they proposed to multiply Φ_0 with a coherence term f_3 as displayed in equation (2.39).

$$I_{\rm SFG} \sim \left| \chi^{(2)} + \chi^{(3)'} \cdot \Phi_0 \cdot f_3 \right|^2 \cdot I_{\rm vis} \cdot I_{\rm IR}$$
(2.39)

However, for concentrations above ~ 1 mM as in this thesis f_3 is approximately one and does not change anymore. Therefore, its impact on the observed intensity can be neglected for the present study.

Within this thesis, the change of the surface potential will be examined by the magnitude of the measured v-SFG intensity. If only relative changes, for instance, upon concentration changes, are directly compared, it is a good approximation to treat the integral over the unnormalized spectrum as the SFG intensity without correction for the Fresnel coefficients or the shape of the IR pulse.^{10,25,33} For the conditions in the mM concentration range, the intensities from the integrated spectra are correlated to the surface potential Φ_0 via equation (2.40).

$$I_{\rm SFG} \sim \left| \chi^{(2)} + \chi^{(3)'} \cdot \Phi_0 \right|^2 \tag{2.40}$$

3 Methods

This chapter describes the methods used within this thesis, which is mainly the laser setup as well as the procedure to conduct flow experiments as well as to evaluate and model the data. Sections 3.1.5, 3.2.2, 3.2.3, 3.3, 3.4.1, and 3.4.2 are extracted and modified from the publication "Liquid flow reversibly creates a macroscopic surface charge gradient", *Nature Communications* **12**, 4102 (2021). Additionally, the modified sections 3.3 and 3.4.1 as well as section 3.4.3 are part of a manuscript that is currently in preparation under the working title "Flow experiments reveal the interplay of different adsorption reactions at a mineral-water interface".

3.1 Experimental Setup

3.1.1 Overview of SFG Setup

A schematic overview of the spectroscopic setup is shown in Fig. 3.1. The source of the used radiation is a commercial 800 nm pulsed laser system. A part of the visible (Vis) radiation at \sim 800 nm is directed to the sample. A second part of the beam is converted to infrared (IR) radiation using a combination of a commercial TOPAS with a Non-collinear Difference Frequency Generation (NDFG) unit attached to it. At the sample, the combination of Vis and IR leads to the evolution of Sum Frequency Generation (SFG) light, which is monitored via a detector.



Fig. 3.1. Overview of spectroscopic setup. Visible (Vis) light (here in blue) is directed to the sample. A part of the light passes a combination of a commercial TOPAS and a Non-collinear Difference Frequency Generation (NDFG) system, leading to infrared (IR) light (here in red). At the sample Sum Frequency Generation (SFG) light (here in violet) arises, which is monitored via a detector.

3.1.2 Generation of Pulsed 800 nm Light

The 800 nm radiation is generated in a Solstice® Ace[™] laser system from Spectra Physics consisting of a seed and a pump laser, a pulse stretcher, a pulse compressor, and an amplifier.¹⁰¹

The output of the pump laser is green light at 527 nm, which excites the laser medium in the amplifier and generates population inversion there. The pump laser itself is pumped by an integrated diode. The green light is the frequency-doubled output from the Nd:YLF (Nd³⁺ ions doped in an yttrium lithium fluoride, YLF crystal) medium.¹⁰¹⁻¹⁰³ Pulsed lasing with a durations of > 50 ns is enabled by Q-switch based on an acousto-optic modulator (AOM).^{102,103}

The seed laser generates ultrafast laser pulses that are used for amplification. The seed laser is based on a Ti:Sapphire (Ti³⁺ ions replace Al³⁺ ions in Al₂O₃) medium that is pumped by a continuous wave diode laser. The Ti:Sapphire medium exhibits broad absorption and emission spectra, which provides flexibility in the excitation wavelength and allows to tune the emission wavelength. Furthermore, the broadness in frequency enables the generation of ultrashort pulses limited by the uncertainty principle from equation (3.1), where Δt is the time width of a pulse and Δv its frequency spread.^{101,104,105}

$$\Delta t \cdot \Delta \nu = \frac{1}{2 \cdot \pi} \tag{3.1}$$

The generation of ultra-short pulses (fs-range) from the seed laser is enabled by mode-locking, where the interference of pulses from different modes (different frequencies) leads to pulses with shorter time widths. An AOM is used for the out-coupling of pulses.^{103,105}

Before a pulse from the seed laser is used to stimulate the emission in the amplifier, the pulses are stretched in time to reduce the power and thereby prevent damage of crystals or other optical elements. This stretching is achieved by delaying one frequency relative to another, e.g. redder light (lower frequencies) travels in time before bluer light (higher frequencies). After the amplification the pulse is recompressed. The elongated pulse duration with frequency-dependent dispersion in time also known as chirp is caused by group velocity dispersion (GVD). A chirp can be implemented by the combination of diffracting gratings and mirrors, causing parts of the dispersed light to travel a longer distance, which leads to a delay and thus a dispersion in time. While the frequencies are spatially recombined by a grating, the pulse is still stretched in time. After the amplification of the chirped pulse, a compressor is used, which works in the opposite way of the stretcher, in order to reduce the time width again.¹⁰¹

The amplifier is like the seed laser based on a Ti:Sapphire medium. After the train of mode-locked pulses from the seed laser is stretched, a pulse selection for the amplification takes place via Pockels cells, which are based on electro-optical materials. The application of a voltage causes the material to become birefringent so that the Pockels cell works as a $\lambda/4$ plate. Therefore, if the beam passes the Pockels cell twice, which is equal to passing a $\lambda/2$ plate, the polarization is changed from horizontal to vertical or vice versa. The combination of

time-controlled Pockels cells and polarizers allows for selecting pulses from the seed laser. Additionally, Pockels cells are used to control the number of round trips within the amplifier.^{101,105}

The Solstice® Ace^m laser system is operated at a repetition rate of 1 kHz for pulses with a duration of ~40 fs. The output power is ~6 W, which is used to supply the Vis pulse for the SFG experiment, input for the TOPAS and NDFG units that convert pulses in the IR range, and another setup, which is not relevant for this thesis.

3.1.3 Conversion of 800 nm Pulses to Broadband IR Pulses

A part of the visible 800 nm light gets converted to IR radiation in a commercial combination of a TOPAS-Prime optical parametric amplifier and an NDFG unit both from Light Conversion.

In the TOPAS, a white light continuum is generated and two times amplified. As a first step, the incoming beam from the 800 nm laser system is split two times, and the smallest fraction is used to generate the white light continuum in a sapphire plate. The recombination of the white light with the other two fractions of the 800 nm light in amplification crystals leads to the enhancement of a certain wavelength. Changing temporal and spatial overlap of the pulses as well as the angle between beams and crystals for the amplification steps allow tuning of the amplified wavelength and thus the output.¹⁰⁶

The optical processes occurring in the TOPAS are non-linear and therefore require pulses of high intensity. The generation of white light in the sapphire plate is due to the interplay of several non-linear processes such as self-focusing or multi-photon absorption.¹⁰⁷ Also, the amplification is a non-linear process. The Signal frequency ω_{Signal} , which is amplified, is lower than the pump frequency ω_{Pump} (here from the 800 nm pulse). In the amplification crystal (β -barium borate, β -BaB₂O₄) the interaction of those two pulses leads to the enhancement of the Signal and the generation of an Idler with the frequency $\omega_{Idler} = \omega_{Pump} - \omega_{Signal}$.¹⁰⁸

Signal and Idler are used for difference frequency generation in the NDFG unit after the TOPAS. Both beams are overlapped in a non-linear DFG crystal (silver gallium sulfide, AgGaS₂), leading to IR radiation at the difference of the frequencies of Signal and Idler. Again, the temporal and spatial overlap of the pulses, as well as the angle between beams and crystals, allow fine-tuning of the yielded frequency. Due to the non-collinearity, the three beams at the outlet of the NDFG unit (Signal, Idler, IR) are separated spatially.¹⁰⁹

3.1.4 Detailed Sample Beam Path

A detailed beam path within the experimental setup after the laser and NDFG unit is depicted in Fig. 3.2a. Over the time of all the experiments that contributed to this thesis, small adjustments to the setup have been made. For instance, a second filter after the NDFG unit has been added.

The Vis beam first passes an 800 nm band pass filter, reducing the power before passing a Fabry-Perot etalon (SLS Optics Ltd.) to decrease the spectral width of the laser pulse to ~20 cm⁻¹. A second 800 nm band pass filter after the etalon filters satellites. Next, a delay stage is used to fine-tune the timing of Vis pulse relative to IR pulses in order to assure temporal overlap of both beams at the sample. To get a focused beam at the sample, a lens with a focal length of 30 cm is used. Before the sample, a combination of two $\lambda/2$ plates and a cube polarizing beam splitter is used to control the power and polarization of the Vis pulse. If needed, the $\lambda/2$ plate before the polarizer can be used to change the ratio of horizontal (h) and vertical (v) polarization and therefore reduce the beam power after the polarizer. H-polarization corresponds to an electric field oscillating parallel to the laser table while v-polarization after the polarizer to the desired one for the experiment. The power of the Vis beam shortly before the sample is usually between 10 and 13 mW.

The IR pulse is separated from Signal and Idler by filters. A combination of one $\lambda/2$ plate and a grid polarizer is used to control the polarization. The IR output of the NDFG unit after the TOPAS is h-polarized. The $\lambda/2$ plate may convert the polarization to v-polarized, and the polarizer ensures a clean polarization. Before the sample, the beam passes a lens with 7.5 cm focal length for focussing. At this position, IR and Vis beams travel in a plane but at different heights. Since only the IR pulse should pass this lens, it is cut so that the Vis beam can travel underneath it. The IR power shortly before the sample is a few mW.

A bridge mirror brings the beams out of the horizontal plane and sends them to the sample with a flat incident angles to enable total internal reflection, as illustrated in the tilted view on the sample in Fig. 3.2b. Due to changes in the alignment, the incident angles vary over the experiments by a few degree from $\theta_{Vis} \approx 74^{\circ}$ and $\theta_{IR} \approx 79^{\circ}$.

After the sample, the beams pass a collimation lens with 15 cm focal length and a 775 nm shortpass filter extracting the SFG radiation. A combination of a $\lambda/2$ plate and a cube polarizing beam splitter controls the polarization that travels to the detector. In front of the detector, the radiation is focused by a lens with 5 cm focal length and is filtered by a second 775 nm shortpass filter to remove possible reflections from the Vis beam.


Fig. 3.2. Detailed beam path. (a) Schematic path (top view) of the Vis, IR, and SFG light. **(b)** Schematic path (tilted view) of the Vis, IR, and SFG light near the sample. Both illustrations are kindly provided by Marc-Jan van Zadel. The optics that are passed by the radiation are labeled according to the radiation in blue, red, or violet letters corresponding to Vis, IR or SFG beams, respectively. Legend: E = Etalon, F = Filter, L = lens, $\lambda/2 = Half$ -wave-plate, PBC = Polarizing beamsplitter cube, P = Polarizer.

Before detection, the SFG light is dispersed for spectral resolution by using a spectrograph (Acton Spectro Pro® SP-2300, Princeton Instruments) with 600 grids per mm. Detection takes place via an electron-multiplied charged-coupled device (emCCD) camera (ProEM 1600, Princeton Instruments). Here the light reaches a chip with 1600x200 pixels made of a metal oxide semiconductor. At every pixel, the incident light can generate an electron-hole-pair due to the internal photoelectric effect. The charge is saved in a capacitor until the read-out. The amount of charge is proportional to the intensity of the incident light, which quantifies the SFG signal. Each of the 1600 pixel columns corresponds to one frequency. The intensity spread over the 1600 pixels corresponds to the spectrum. In height, the signal ranges over several pixels,

which is why they are combined (binned). Binning is applied over 31 of the 200 pixels per frequency.^{103,110,111}

All spectra of the fluorite-water interface are recorded in ssp polarization combination (spolarized SFG, s-polarized Vis, and p-polarized IR). Spectra of a gold-coated fluorite prism are recorded in either ppp polarization for optimizing the alignment and calibrating the wavenumbers (see section 3.3) or ssp polarization for spectra normalization (see section 2.4.4).

3.1.5 Flow Setup

The spectroscopically studied sample is the fluorite-water interface with and without applied flow of the aqueous phase. A scheme of the flow setup and technical drawings of the flow cell in different views are shown in Fig. 3.3. The design of the flow cell has been optimized with the kind help of Marc-Jan van Zadel to favor the laminarity of the flow. The rectangular prism is mounted on top of the flow channel. A 0.03 mm Teflon film is used for sealing. The flow rate studied is usually between 1 and 6 mL·min⁻¹, corresponding to a Reynolds numbers of $\sim 5 - 25$ and shear rates of ~ 1.5 to 9 s⁻¹, which additionally ensures laminar flow over the investigated flow cell. Only in chapter 7 flow rates up to ~ 600 mL·min⁻¹ are investigated. A reservoir with ~ 100 mL of the solution is connected with the flow cell via Tygon® tubes (ISMCSC0832 MHSL 2001; inner diameter 4.8 mm, outer diameter: 8.0 mm). The peristaltic pump (Masterflex 77924-70 L/S Ethernet/IP Network-Compatible Pump) is controlled by a self-written LabView program.). Jürgen Worm kindly provided this program. The same program controls the motors (Newport Spectra-Physics GmbH CONEX-TRA25CC) of the x- and y-stages (Manual Linear Stage, Crossed-Roller Bearings, 25.4 mm Travel, M6).

3.2 Experiments

3.2.1 Chemicals

The salts used are listed and specified in Table 3.1. Concentrated hydrochloric acid is purchased from VWR (37 w%). Usually, reagents are used as received without further purification. Only for two experiments, rubidium chloride has been baked at ~500°C overnight before it is dissolved.



Fig. 3.3. Illustration of flow setup. (a) The flow cell has a flow channel with a rectangular fluorite prism mount on top. The Vis and IR laser pulse overlap at the center of the flow channel and generate SFG light in total internal reflection geometry. The flow cell is connected to a reservoir and a peristaltic pump. **(b)** Technical drawings of the flow cell with dimensions in mm. Top panel shows a top view. A and B indicate the cross-sections shown in the middle and bottom panel, respectively. Both parts of this figure are produced with the kind help of Marc-Jan van Zadel.

Salt	Supplier	Purity
Lithium chloride	Carl Roth	≥99.5%
Sodium chloride	Carl Roth	≥99.5%
Potassium chloride	Sigma-Aldrich	≥99.5%
Cesium chloride	Carl Roth	≥99.999%
Magnesium chloride hexahydrate	Carl Roth	≥99%
Calcium chloride dihydrate	Sigma	99%
	Carl Roth	≥99%
Sodium fluoride	Merck	≥99.99%
Sodium bromide	Sigma-Aldrich	≥99.0%
	Carl Roth	≥99%
Sodium iodide	Alfa Aesar	≥99.5%
Sodium thiosulfate	Carl Roth	≥99%
Sodium hydroxide	Sigma-Aldrich	98-100%

 Table 3.1 Overview of salts used. For each salt, the supplier and the purity are specified.

3.2.2 Sample preparation

The rectangular fluorite prism (dimensions $4 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ cm}$) purchased from EKSMA Optics is baked at ~500 °C for at least 2 h to remove organic residues. Cooling down of the oven usually takes ~6 hours. Before and after baking, it is rinsed with demineralized water (Milli-Q), filtered with a Millipore unit (resistivity = $18 \text{ M}\Omega \text{ cm}$). After rinsing the prism, it is stored in Milli-Q water until it is used for the experiment. Acidic solutions with added salts are prepared

by adding the salt to a pH 3 solution of hydrochloric acid prepared from the concentrated acid and Milli-Q water. Usually, a concentration series was prepared via a dilution series. Acidic solutions with different pH are prepared by diluting concentrated hydrochloric acid with Milli-Q water. Solutions with alkaline pH are prepared by dissolving sodium hydroxide in Milli-Q water.

3.2.3 Experimental Procedure

One of the two motorized stages is used to bring the center of the flow channel perpendicular to the flow direction into the focus of the incident laser beams. To do so, a prism with 100 nm gold coating in the area of the flow channel is mounted on the flow cell, and the stage is moved to the edges of the gold coating where the gold SFG signal in ppp polarization combination disappears. Here, the CCD chip is binned over all 200 pixels in height. The center is chosen in the middle of the edges. The middle of the flow channel in flow direction was marked with an engraving on the flow cell's surface. The second stage, orthogonal to the first one, is used to adjust the laser focus to the center of the flow cell in flow direction by eye with the help of the engraving. At the center, binning is limited to the region of the signal (31 pixels in height with the signal centered). To determine the region of binning, an image of the chip is recorded. Moreover, reference spectra are recorded with the gold-coated prism. In ppp polarization combination, one spectrum of the gold-coated prism is recorded, another one with the IR beam blocked, and another one with a polystyrene foil in the IR beam path. Those spectra were usually recorded over 1 s each. Additionally, one spectrum in ssp polarization combination with and one without blocked IR beam are recorded, usually over 100 s. Those spectra are not recorded for the data discussed in chapter 4. After recording the reference spectra, the flow cell and the tubes are rinsed with Milli-Q water. Before spectra of the fluorite-water interface are collected, the flow cell with the freshly cleaned prism mounted is flushed for 2 min at a high flow rate of ~600 mL·min⁻¹ with the solution, followed by at least 5 min of rest to ensure equilibration of the interface. The second stage is used to change the position along the flow direction if required in the experiment. If not stated otherwise, measurements were conducted at the center of the flow channel. Usually, spectra are recorded with an acquisition time of 5 s for continuous measurements over time. However, when the flow rate is changed after each spectrum in chapter 7, the acquisition time is reduced to 2 s. For solely studying flow-off spectra at different fluoride concentrations and different pH in chapter 5, the acquisition time is 10 s. The single spectra used to illustrate the local field correction in section 2.4.4 are acquired over 20 s (pH 3) or 60 s (pH 14).

3.3 Data Processing

The spectra are subtracted by a background obtained by measuring a spectrum with the IR beam blocked for the same time as for the usual spectrum. Cosmic rays are identified by a self-written MATLAB script once a tolerance for the difference between the intensities of neighboring pixels is exceeded. The cosmic ray is replaced by the average of the intensities from the two pixels at lower wavelengths. Usually, a spectrum of 1600 data points contains less than 1% of cosmic rays. The ppp reference spectrum of gold with polystyrene in the IR beam path exhibits dips due to the infrared absorption of the foil. The absorption dips are used for calibrating the wavenumbers. Integration of the spectra is done by summation of the background-subtracted intensities. The integration range covers the region of the IR pulse, which differs between days. The integration range in the MATLAB script was adapted several times throughout the course of all experiments to ensure that the whole signal is integrated. However, direct comparisons are done only for data processed in the same way. In some cases, the range exceeds the region of the IR pulse, which for a background-subtracted spectrum does not lead to significant changes, but it was within 2500 to 4000 cm⁻¹.

Plotting the integrated spectra over time leads to time traces of the v-SFG intensity, as shown in Fig. 3.4. In chapter 4, the relative change of the v-SFG signal upon flow is rather high, as shown in Fig. 3.4a. In some experiments with lower changes upon flow that contribute to chapters 5 and 6, the v-SFG intensity shows a significant long-term development, on top of which the flowinduced changes occur. This long-term development is not correlated with the investigated fluoride concentration as shown in Fig. 3.4b and Fig. 3.4c, which are both obtained with the same fluoride concentration, but the long-term development (background change) is only present in Fig. 3.4c. Moreover, this background change can appear as both, increasing intensity as in Fig. 3.4c or decreasing intensity as in Fig. 3.4d. This underlying development of the intensities has more influence, when the intensities and the flow-induced changes are smaller, as it is the case for the conditions chosen in chapters 5 and 6. Since this process is unspecific, it might be due to laser fluctuations. However, a long-term process occurring at the surface might also be an explanation. In order to disentangle the unspecific development from the flow-induced changes, a linear correction of the intensities can be applied. This correction is done by aligning the flow-off states before and after the flow-on period to the intensity of the very first spectrum, as shown in Fig. 3.4c and d. Spectra over ~ 2 min before starting flow were considered for the linear correction. After the correction, relative changes of the signal upon flow are calculated. For the experiments that contribute to chapter 4, relative changes upon flow are calculated by averaging spectra over ~ 5 min prior to starting the flow and spectra over ~ 5 min prior to turning the flow off. Those regimes are marked in Fig. 3.4a. For the data presented in chapters 5 and 6, the averaging time is reduced to ~ 1 min as shown in Fig. 3.4b, due to the necessity of the correction.



Fig. 3.4. Correction of v-SFG intensities. V-SFG intensity development during two flow-on/off cycles for a fluorite prism in contact with a pH 3 HCl solution and an added amount of sodium chloride or sodium fluoride as indicated in the figure. Each open black circle represents one integrated spectrum. The solid colored lines are ten-point moving averages to guide the eye. The bottom panels show the applied flow rates (solid black lines). **(a)** The difference in intensity between the flow-off regimes is small compared to the flow-induced change. **(b)** The intensities of the flow-off regimes reach the same level. Therefore, no long-term effect seems to be present. The intensity trace was not corrected. The blue and red lines highlight the regions at the end of a flow-off and flow-on interval, respectively. Those regions are taken to calculate relative changes upon flow. **(c)** The intensities of the flow-off regimes do not reach the same level (top). A linear correction between the first two flow-off intervals is applied over the whole experiment. The grey lines highlight the regions at the end of the flow-off intervals that are used for a linear fit (solid black line) that corrects for the underlying increase that is corrected for. The corrected intensity trace is shown in the middle panel. **(d)** Same as (c), but this time, there is an underlying decrease that only persists until the second half of the flow-on/off experiment.

3.4 Modelling

3.4.1 Implementing the Langmuir Model

The base of modelling the v-SFG intensities and their change upon flow is the connection of the v-SFG intensity to the surface charge via the surface potential with the equations (2.6) and (2.40). The surface charge can be described by Langmuir adsorption/desorption of ions based on the discussion in section 2.1. This description was initiated and implemented by Willem Q. Boon within the modeling contributing to chapter 4.

The adsorption/desorption of fluoride ions on the fluorite surface and its connection to a positive surface charge is expressed in equation (3.2), where \equiv represents the underlying solid phase.

$$\equiv CaF_2(s) \rightleftharpoons \equiv CaF^+(s) + F^-(aq)$$
(3.2)

According to equation (3.2), a surface site can be either one time positively charged (\equiv CaF⁺) or uncharged (\equiv CaF₂). Thus, the density of surface sites Γ is split according to equation (3.3). Given the crystal structure¹¹² Γ is roughly 10 nm⁻².

$$\Gamma = \Gamma_{\equiv CaF_2} + \Gamma_{\equiv CaF^+} \tag{3.3}$$

The surface charge (density) is simply $\Gamma_{\equiv CaF^+}$ multiplied with the elementary charge *e*. Under steady state conditions, the time derivative of the surface charge $d\sigma/dt$ is zero (equation (3.4)), and the adsorption and desorption reactions are in equilibrium. Experimentally, this is observed by a constant v-SFG response. The equilibrium surface charge is given by equation (3.5).

$$\frac{d\sigma}{dt} = e \cdot \left(-k_{\mathrm{ads},\mathrm{F}} \cdot c_{\mathrm{F}} \cdot \Gamma_{\equiv\mathrm{CaF}^{+}} + k_{\mathrm{des},\mathrm{F}} \cdot \Gamma_{\equiv\mathrm{CaF}_{2}}\right) = 0 \tag{3.4}$$

$$\sigma = \frac{e \cdot \Gamma}{1 + \frac{k_{\text{ads},F}}{k_{\text{des},F}} \cdot c_{\text{F}}}}$$
(3.5)

While this model of the surface charge is sufficient for the discussions in chapter 4, an additional adsorption/desorption reaction is added in chapter 5. For this extension, a competition between the adsorption/desorption reactions of fluoride ions (equation (3.2)) and calcium ions (equation (3.6)) is assumed. Note that the uncharged terminal CaF₂ site can be considered part of the solid subphase (\equiv) when a calcium ion adsorbs. Inversely, once a terminal Ca²⁺ group is desorbed, the underlying CaF₂ unit from the solid phase becomes the terminal surface site, which is uncharged.

$$\equiv \operatorname{CaF}_2(s) + \operatorname{Ca}^{2+}(\operatorname{aq}) \rightleftharpoons \equiv \operatorname{Ca}^{2+}(s)$$
(3.6)

Based on equations (3.2) and (3.6), a surface site can be uncharged (\equiv CaF₂), one time positively charged (\equiv CaF⁺) or two times positively charged (\equiv Ca²⁺), which is why the density of surface sites splits up according to equation (3.7).

$$\Gamma = \Gamma_{\equiv CaF_2} + \Gamma_{\equiv CaF^+} + \Gamma_{\equiv Ca^{2+}}$$
(3.7)

The surface charge is not only determined by the fluoride vacancies $\equiv CaF^+$ but also the other charged terminal $\equiv Ca^{2+}$ groups as in equation (3.8), leading to the time derivative of the surface charge in equation (3.9), which is in a steady state again zero.

$$\sigma = e \cdot (\Gamma_{\equiv CaF^+} + 2 \cdot \Gamma_{\equiv Ca^{2+}}) \tag{3.8}$$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = e \cdot (-k_{\mathrm{ads},\mathrm{F}} \cdot c_{\mathrm{F}} \cdot \Gamma_{\equiv\mathrm{CaF}^{+}} + k_{\mathrm{des},\mathrm{F}} \cdot \Gamma_{\equiv\mathrm{CaF}_{2}} + 2 \cdot k_{\mathrm{ads},\mathrm{Ca}} \cdot c_{\mathrm{Ca}} \cdot \Gamma_{\equiv\mathrm{CaF}_{2}} -2 \cdot k_{\mathrm{des},\mathrm{Ca}} \cdot \Gamma_{\equiv\mathrm{Ca}^{2+}}) = 0$$

$$(3.9)$$

The limitation to the three possible surface species ($\equiv CaF_2$, $\equiv CaF^+$, $\equiv Ca^{2+}$) is consistent with the shape of the v-SFG spectrum in the OH-stretch region shown in Fig. 2.6d. This spectral shape suggests a net positively charged surface. If there were a change to a net negatively charged surface, one would see a clear change of the OH-stretch band in the v-SFG spectra as in Fig. 2.3, which is not observed in the spectra for the different fluoride concentrations in chapter 5. Additionally, a change in the sign of the surface charge would require a minimum in the intensity when passing the point of zero charge¹⁰ rather than just a decrease in the intensities. However, the v-SFG spectra only report on an averaged orientation of the water molecules. Therefore, only information on the net charge is accessible, so it might still be possible that additional reactions and other surface species are present. For instance, fluoride adsorption at an uncharged site could occur, leading to a one times negatively charged site. Moreover, a direct conversion between a one times positively charged ($\equiv CaF^+$) and two times positively charged ($\equiv Ca^{2+}$) surface site via another fluoride adsorption/desorption reaction would be plausible. Such additional reactions or surface sites are neglected for simplicity.

In equilibrium, adsorption and desorption are balanced, and the density of the different surface sites stays constant, which leads to the equations (3.10) and (3.11).

$$\frac{d\Gamma_{\equiv CaF^+}}{dt} = -k_{\mathrm{ads},\mathrm{F}} \cdot c_{\mathrm{F}} \cdot \Gamma_{\equiv \mathrm{CaF^+}} + k_{\mathrm{des},\mathrm{F}} \cdot \Gamma_{\equiv \mathrm{CaF_2}} = 0$$
(3.10)

$$\frac{d\Gamma_{\equiv Ca^{2+}}}{dt} = k_{\mathrm{ads,Ca}} \cdot c_{\mathrm{Ca}} \cdot \Gamma_{\equiv CaF_2} - k_{\mathrm{des,Ca}} \cdot \Gamma_{\equiv \mathrm{Ca}^{2+}} = 0$$
(3.11)

The equations (3.7)-(3.11) form a set of linear equations. Solving this for the surface charge σ leads to equation (3.12), which is used for the extended adsorption/desorption model in chapter 5.

$$\sigma = \frac{\mathbf{e} \cdot \Gamma}{1 + \frac{k_{\mathrm{ads,F}}}{k_{\mathrm{des,F}}} \cdot c_F + \frac{k_{\mathrm{ads,F}}}{k_{\mathrm{des,F}}} \cdot \frac{k_{\mathrm{ads,Ca}}}{k_{\mathrm{des,Ca}}} \cdot c_F \cdot c_{\mathrm{Ca}}} + \frac{2 \cdot \mathbf{e} \cdot \Gamma}{1 + \frac{k_{\mathrm{des,Ca}}}{k_{\mathrm{ads,Ca}}} \cdot \frac{1}{c_{\mathrm{Ca}}} + \frac{k_{\mathrm{des,Ca}}}{k_{\mathrm{ads,Ca}}} \cdot \frac{1}{c_{\mathrm{Ca}}} \cdot \frac{k_{\mathrm{des,F}}}{k_{\mathrm{ads,F}}} \cdot \frac{1}{c_F}}$$
(3.12)

3.4.2 Numerical Simulations of the Flow Setup

In chapter 4, the results of numerical simulation of the flow setup are presented. To this end, Willem Q. Boon simulated a cylindrical flow channel in the commercial finite-element software package COMSOL MULTIPHYSICS. In the simulation, cylindrical coordinates (x, r, θ_c) are used and azimuthal symmetry is assumed. A sketch of the flow channel in the simulation is shown in Fig. 3.5.



Fig. 3.5. Illustration of the flow setup in the simulation. Projection on the cylindrical flow setup in the simulation, which is not true to scale. The x-direction corresponds to the direction of flow. The centered flow channel is connected to two reservoirs, each $L_R = 42$ mm long and with a radius of $L_R = 42$ mm. The flow channel has a length of $2 \cdot L_C = 40$ mm and is in contact with the $2 \cdot L_S = 24.8$ mm long fluorite surface. The channel has a diameter of $2 \cdot R = 4.8$ mm.

The origin is located at the center of the channel. The radius of the channel is R = 2.4 mm, and the channel runs from $x = -L_C$ to $x = +L_C$ with $L_C = 20$ mm. The fluorite surface is located

between $x = -L_S$ and $x = +L_S$ with $L_S = 12.4$ mm. Two bulk reservoirs of the radius and length $L_{\rm R} = 42 \text{ mm}$ are connected to the channel. As boundary conditions, the bulk concentrations $c_i(-L_b) = c_i(L_b) = c_{i,b}$ at the reservoir in- and outlet are imposed. In the experiment, the bulk concentrations correspond to a pH 3 HCl solution with 1 mM NaCl and 1 μ M NaF added. The simulation considers everywhere $c_{\text{Na}}(x,r) + c_{\text{H}}(x,r) = c_{\text{Cl}}(x,r) = 2 \text{ mM}$ and $c_{\rm F}(x,r) = 2 \cdot c_{\rm Ca}(x,r)$. One should note that for fixing the fluoride bulk concentration, NaF is used in the experiment instead of CaF_2 leading to a small discrepancy in the calcium concentration. At the fluorite-water interface (wall of the flow channel), an adsorption/desorption reaction of fluoride anions (equation (3.2)) determines the surface charge, and a dissolution reaction (equation (3.13)) provides a flux of fluoride and calcium ions.

$$\equiv \operatorname{CaF}_2(s) \rightleftharpoons \equiv \operatorname{CaF}_2(s) + 2F^{-}(\mathrm{aq}) + \operatorname{Ca}^{2+}(\mathrm{aq})$$
(3.13)

At the remaining channel wall, no reactions occur. The adsorption/desorption is described by the equation (3.5) with $k_{ads}/k_{des} = 10^4 \text{ m}^3 \cdot \text{mol}^{-1}$ and $\Gamma = 10 \text{ nm}^{-2}$. The flux of fluoride anions is described by equation (3.14).

$$\boldsymbol{n} \cdot \boldsymbol{J}_{\mathrm{F}}(x) = 2 \, k_{\mathrm{dis}} \left(1 - \frac{k_{\mathrm{prec}} c_{\mathrm{F}}^3(x, R)}{2 \, k_{\mathrm{dis}}} \right) = D \cdot \frac{d}{dr} c_{\mathrm{F}}(x, r) \,|_{r = R}$$

$$(3.14)$$

Here, **n** is the surface normal vector, D the diffusion coefficient, which is assumed to be the same for all ions, and k_{dis} and k_{prec} are the rate constants for dissolution and precipitation, respectively. The dissolution process with $k_{dis} = 0.027 \,\mu \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ is limited by the saturation concentration $c_{F,sat} = 10 \,\mu \text{M}.^{13,113,114}$ Due to the stoichiometry of fluorite (CaF₂), the flux of fluoride ions is twice that of calcium ions $J_F = 2 \cdot J_{Ca}$ and therefore, $c_F(x,r) = 2 \cdot c_{Ca}(x,r)$. The diffusion coefficient is approximated with $D = 10^{-9} \,\text{m}^2 \cdot \text{s}^{-1}$, which is a typical order of magnitude for ions in aqueous solutions.⁴¹

Under flow conditions, the stream profile is described by the Navier-Stokes equation, and mass transport needs to be taken into account. As discussed in sections 2.3.1, several simplifications as no-slip boundary conditions at the channel wall ($\mathbf{u}(R) = 0$) leads to the parabolic Poiseuille profile from equation (2.11), which is applied here. The viscosity, which influences that profile, is approximated with $\eta = 10^{-3}$ Pa·s as a typical order of magnitude for aqueous solutions.⁴¹

While at the fluorite-water interface, chemical reactions are considered as explained above, mass transport in the solution (flow channel) is limited to diffusion and advection, simplifying equation (2.14) to equation (3.15).

$$\frac{dc_i}{dt} = -div(c_i \cdot \boldsymbol{u}) + D_i \cdot div(grad(c_i))$$
(3.15)

Within the simulations, electrostatics are neglected as they would require a nm-scale resolution that is computationally intractable on the cm-scale of the flow channel.

The simulation provides the concentration profiles of the dissolved ions under flow-off and flow-on conditions. Additionally, the interfacial concentration is connected to the dissolution rate and the density of charged groups due to the adsorption/desorption of fluoride. The latter can be converted to a surface charge, which according to equations (2.6) and (2.40) is connected to the surface potential and thus the v-SFG intensity. For simplicity, only a scaling with the surface potential is considered, i.e., $\chi^{(2)} = 0$.

3.4.3 Modeling Concentration Series

In chapter 5, the dependency of the v-SFG intensity and its change upon flow on the fluoride bulk concentration is modelled with a Langmuir adsorption model similar to the one described in the previous section. For this part, however, only one position in the flow channel is investigated, which is why there is no need to simulate the full flow setup. The modelling is performed via a self-written MATLAB script. As in the previous section, flow-off concentrations at the interface are assumed to be saturation concentrations. Due to the large range of fluoride bulk concentrations between 0 and 3 mM, which is set by adding NaF, $c_F(x,r) = 2 \cdot c_{Ca}(x,r)$ is no longer a valid assumption. It is rather assumed that CaF₂ dissolves until the concentration product is reached according to equation (3.16) where x_{CaF_2} is the amount of dissolved fluorite. While in the previous section, a saturation concentration has been considered that corresponds to a concentration reached after several hours, here complete saturation, at least close to the interface, shall be approached. Thus, the system is modeled with the solubility product $L_{CaF_2} = 3.45 \cdot 10^{-2} \text{ mol}^3 \cdot \text{m}^{-9.112}$ The bulk calcium concentration is assumed to be zero.

$$L_{\text{CaF}_2} = c_{\text{F}}^2 \cdot c_{\text{Ca}} = \left(c_{F,b} + 2x_{CaF_2}\right)^2 \cdot x_{CaF_2}$$
(3.16)

The bulk concentration is not simply the added amount of fluoride $c_{F,0}$, as it needs to be corrected for the formation of HF according to the equilibrium from equation (3.17) with the pK_a of 3.2.¹¹² The corrected concentration is calculated based on equation (3.18) with $c_{H,0}$ as the initial proton concentration corresponding to a pH of 3. The proton concentration changes accordingly.

$$\mathrm{H}_{(aq)}^{+} + F_{(aq)}^{-} \rightleftarrows \mathrm{HF}_{(aq)}$$

$$(3.17)$$

$$c_{F,b} = c_{F,0} - \frac{c_{F,0} + c_{H,0} + 10^{-pK_a}}{2} + \sqrt{\left(\frac{c_{F,0} + c_{H,0} + 10^{-pK_a}}{2}\right)^2 - c_{F,0} \cdot 10^{-pK_a}}$$
(3.18)

The presence of flow dilutes the solution in the flow channel with the bulk solution from the reservoir. Therefore, the concentration upon flow c_{On} must be between the flow-off concentration c_{Off} and the bulk concentration. The flow condition is incorporated by an effective dilution δ according to equation (3.19). An adequate dilution is $\delta = 0.35$, which is close to the change in concentration that can be obtained with the numerical calculations from section 3.4.2.

$$c_{\rm On} = c_{\rm Off} \cdot (1 - \delta) + c_{\rm b} \cdot \delta \tag{3.19}$$

With the accessibility of concentrations, the series of v-SFG intensities and their change upon flow are modeled similar to the previous section by assuming Langmuir adsorption/desorption of ions under the neglect of electrostatics. The surface charge is first converted to the surface potential and then to a v-SFG intensity. For a series of added fluoride concentrations labeled with the index *i*, the flow-off intensities are normalized to the one with zero added fluoride (i = 1). Thus, the flow-off intensities were fitted according to equation (3.20), where a $\chi^{(2)}$ -contribution is taken into account. However, as a fit parameter, the ratio $\chi^{(2)}/\chi^{(3)'}$ reaches rather low values of only a few mV. Additionally, a pH-dependency of the v-SFG intensities needs to be incorporated since HF formation is increasing the pH, which is known to decrease the v-SFG intensity for the fluorite-water interface in the acidic pH regime.¹⁰ The correction function f_{corr} is based on a linear fit through the decreasing v-SFG intensities from a pH series between pH 3 and 3.5, which is approximately the pH range captured upon the addition of fluoride within our experiments. For the whole series denoted by the index i the pH is calculated based on HF formation.

$$I_{\text{norm},i} = \frac{\left(\chi^{(2)}/\chi^{(3)'} + \Phi_0(c_{\text{F},i,\text{Off}})\right)^2}{\left(\chi^{(2)}/\chi^{(3)'} + \Phi_0(c_{\text{F},i=1,\text{Off}})\right)^2} \cdot f_{\text{corr}}(\text{pH}_i)$$
(3.20)

Similarly, the flow-induced change was fitted with the function from equation (3.21), which relates the flow-on to the flow-off intensity

$$\left(\frac{I_{\rm On} - I_{\rm Off}}{I_{\rm Off}}\right)_i = \frac{\left(\chi^{(2)}/\chi^{(3)'} + \Phi_{0,\rm On}(c_{\rm F,i,\rm On})\right)^2}{\left(\chi^{(2)}/\chi^{(3)'} + \Phi_{0,\rm Off}(c_{\rm F,i,\rm Off})\right)^2} - 1$$
(3.21)

For modeling $\Gamma = 10 \text{ nm}^{-2}$ is taken as the total density of surface sites. The ratio of the rate constants for both fluoride adsorption/desorption as well as calcium adsorption/desorption were adjusted to describe the experimental data and to match the reported surface potential of 70 mV at pH 3 with zero added fluoride.¹³ The last step of modeling was to optimize the

 $\chi^{(2)}/\chi^{(3)'}$ ratio within the limitation of a positive sign. In chapter 5, the inverse $(\chi^{(3)'}/\chi^{(2)})$ is referred to since this value is more common in literature. The best model of the data and the surface potential discussed in chapter 5 is obtained using $k_{ads,F}/k_{des,F} = 700 \text{ m}^3 \cdot \text{mol}^{-1}$, $k_{ads,Ca}/k_{des,Ca} = 0.005 \text{ m}^3 \cdot \text{mol}^{-1}$, and $\chi^{(3)'}/\chi^{(2)} = 250 \text{ V}^{-1}$. The discrepancy between the values here and within the numerical simulation is connected to the higher solubility used in this model, as it has become evident that this is more suitable.

4 Flow-induced Surface Charge Gradient

LIS et al.¹⁰ and SCHAEFER et al.³³ found that liquid flow can alter interfacial concentrations at mineral-water interfaces. This change affects the surface potential and the orientation of interfacial water molecules as observed via the v-SFG intensity. This chapter characterizes the impact of flow further by following the approach of LIS et al.¹⁰ for the fluorite-water interface at several positions along the flow channel. Besides the v-SFG experiments, we performed numerical simulations of the flow channel and modeled the coupling of mineral dissolution and fluoride adsorption/desorption as surface charging process. This chapter is extracted and modified from the publication "Liquid flow reversibly creates a macroscopic surface charge gradient", *Nature Communications* **12**, 4102 (2021).

At the fluorite-water interface under acidic conditions, LIS et al.¹⁰ found an increase in the v-SFG intensity upon flow, which has been correlated to an increasing surface charge. The change of the surface charge upon flow was argued to be due to the dilution of reactive ions partaking in the surface adsorption/desorption reaction.¹⁰ This dilution is caused by the concentration difference between the fresh solution from the reservoir and that in the flow channel. The dilution changes the adsorption/desorption equilibrium and increases the surface charge, which manifests itself by an increase in the v-SFG response. A similar explanation has also recently been given by XI et al.²¹. Even though the flow-induced disturbance of the charging equilibrium qualitatively explains several experimental features, there are also inconsistencies. For instance, the question remains how a concentration difference between the reservoir and channel is generated. The surface adsorption/desorption reaction itself cannot supply the excess of ions in the channel over the bulk concentration, as the number of reactive ions on the surface is too small to support a steady flux of ions, especially over many flow cycles. Therefore, a fully self-consistent quantitative model is missing. In fact, several different hypotheses have been put forward for the change of the v-SFG signal upon flow, for instance, a surface conduction model by WERKHOVEN et al.,¹¹⁵ which would lead to a surface charge gradient and a 1D toy model by LIAN et al.¹¹⁶ that considers net dissolution as the driving force. A flowdependent surface charge not only paves the way for novel electrokinetic effects,¹¹⁷ but it also has important consequences for the interpretation of zeta potential measurements. However, the mechanism by which the flow alters the surface charge is poorly understood as of yet.¹¹⁸

In this chapter, we investigate the flow-dependent surface potential by measuring v-SFG spectra at several positions in a channel with a length of 2.48 cm and a radius of 0.24 cm as shown in section 3.1.5. The local changes in the surface potential upon flow are tracked through the

intensity of the OH-stretch band in v-SFG spectra, which reports on the alignment and polarization of interfacial water molecules.

4.1 Flow-induced Change in Surface Charge

Similar to LIS et al.¹⁰ and XI et al.²¹, we conducted flow experiments at the fluorite-water interface under acidic conditions, first at a single position in the channel. Fig. 4.1a illustrates our experiment. Visible (Vis) and infrared (IR) laser pulses overlap in space and time at the Fluorite-water interface, such that a nonlinear optical v-SFG process generates a response at a frequency equal to the sum of the two incident frequencies. Due to spectroscopic selection rules, this process is forbidden in centrosymmetric media such as bulk water. In contrast to the bulk, centrosymmetry is broken at the interface, which renders the v-SFG signal interface-specific^{23,24}. Moreover, the resonance of the IR pulse with the water stretching mode at around 3300 cm⁻¹ enhances the overall process and provides additional molecular specificity.^{10,25-32,119}

Our measurements are performed in total internal reflection geometry to increase the signal and reduce the acquisition time, allowing time resolution on a ~second time scale. Fig. 4.1b shows two v-SFG spectra of the fluorite-water interface for a 1 mM NaCl and 1 mM HCl (so pH 3) solution, once under flow-off and once under flow-on conditions. The measured signal is plotted vs. the wavenumber of the IR pulse being in resonance with the OH-stretch vibration of water molecules. The flow-on (red) spectrum in Fig. 4.1b is ~40% higher in intensity compared to the flow-off (blue) spectrum in Fig. 4.1b. This increase can be correlated to an increase in surface charge, as discussed in section 2.4.5. Thus, we reproduced that flow increases the surface charge at the fluorite-water interface under acidic conditions.^{10,21} The underlying mechanism for the flow-induced increase in the surface charge will be considered in section 4.3. When we calculate the intensity of the two spectra of Fig. 4.1b by integrating over the spectral area, we can track their time-dependence upon switching on and off the flow with a resolution of seconds, shown in Fig. 4.1c, where each black circle stems from one spectrum. We note that the v-SFG response is constant before the liquid flow is switched on, which therefore represents a steady state. Upon applying flow, another steady state with an increased v-SFG response is reached within a few min. When the flow is turned off again, the initial steady state is restored but only after about ~10 min. As explained above, the v-SFG response can be used as a measure for the surface charge. Thus, the flow-induced change in the v-SFG signal can be correlated to a reversible

change in surface charge due to flow. The observation of reversible changes in the v-SFG response and thus in surface charge due to liquid flow is consistent with the studies of LIS et al.¹⁰ and XI et al.²¹



Fig. 4.1. Studying the fluorite-water interface by v-SFG. (a) Illustration of the measurement method. In vibrational Sum Frequency Generation (v-SFG) spectroscopy, a visible (Vis) and infrared (IR) pulse overlap in space and time at the interface of interest, generating radiation at the sum of the frequencies (SFG). If an IR pulse is in resonance with the OH stretch vibration of water molecules, the obtained v-SFG spectra provide information on the orientation and polarization of interfacial water molecules. The illustration shows water molecules for the first few hydration layers as well as a schematic distribution of arbitrary ions (anions in yellow, cations in green). At the charged fluorite-water interface, the orientation and polarization of the interfacial water molecules is determined by the surface charge. Thus, the v-SFG signal can be used as an indirect measure for the surface charge. **(b)** v-SFG spectra in arbitrary units (arb. units) in the OH stretch region of the fluorite-water interface at pH 3 (1mM HCl and 1 mM NaCl) under flow-off conditions (blue) and flow-on conditions (red). **(c)** Time trace of integrated SFG spectra (black circles) at the fluorite-aqueous solution interface at pH 3 (1mM HCl and 1 mM NaCl) with one flow on-off cycle (black curve). Each circle represents one spectrum, integrated between 2650 and 3600 cm⁻¹. The solid orange line is a ten-point moving average to guide the eye. The vertical blue and red lines highlight the steady state regimes for flow-off and flow-on conditions. As the intensities are hardly changing over time, a steady state can be assumed.

4.2 Observation of a Flow-induced Surface Charge Gradient

In order to gain an understanding of the interfacial events along the mineral surface upon flow, we compare the changes in v-SFG response at different positions along the flow channel. Another approach is to compare the change in v-SFG signal upon flow at one position, which is not the center of the flow cell, and reversing the flow direction, i.e., interchanging the role of the inlet and outlet as illustrated in Fig. 4.2a. Following the second approach, time traces of the integrated v-SFG spectra at three different positions with flow on/off cycles in clockwise and counter-clockwise flow directions are shown in Fig. 4.2b. First of all, it can be seen that the v-SFG response increases upon flow at every position. Additionally, we observe that at the center of the flow channel (orange spot and trace in Fig. 4.2) essentially identical changes of the v-SFG intensity for both flow directions are observed, which is fully consistent with the study of LIS et al.¹⁰ Here we do not obtain additional spatial information as reversing the flow direction interchanges the center with itself due to the flow cell's symmetry. In contrast, at the two opposite sites at equal distance from the center (8 mm), the reversible changes upon flow depend on the flow direction. At a clockwise flow direction, the increase in the v-SFG response at the red position in Fig. 4.2 is substantially and reproducibly higher than at a counterclockwise flow direction, while the opposite is the case at the other side of the flow cell (blue spot and blue trace). We also note that the magnitude of the increase in v-SFG response in the center is approximately in between that at the inlet and outlet. Thus, we conclude that the increase in the v-SFG response upon flow decreases in the flow direction, such that our measurements show that along the flow channel there is a flow-induced surface charge gradient at the mineral surface in the flow direction.

To further investigate the proposed gradient along the flow channel, we quantitatively compare the flow-induced changes at different positions along the centimeter-sized flow channel for the same flow direction. To do so, we focus on the relative increase of the v–SFG response under flow-on conditions (compared to flow-off) as a function of the distance from the center of the channel. Additionally, we study the influence of the flow rate. The relative increase in v-SFG intensity $(I_{0n} - I_{0ff})/I_{0ff}$ accounts for slight changes in the alignment that necessarily occur when changing the position of the flow cell. The position-dependent relative increase in intensity is determined by averaging the intensity in steady states, as indicated by the marked regimes in Fig. 4.1c. The obtained data are shown in Fig. 4.3, revealing that the intensity throughout the channel increases in the flow-on state, the more so at higher flow rates and closer to the inlet, up to 45% at the inlet for the highest flow rate of 6 mL·min⁻¹ (shear rate \sim 9 s⁻¹) that we consider here. Note, however, that the intensity also increases significantly, by about 15%, at the outlet at the lowest flow rate of 1 mL·min⁻¹ (shear rate \sim 1.5 s⁻¹). With these flow rates, we capture a laminar flow with corresponding Reynolds numbers between \sim 5 and \sim 25. For each flow rate, the increase of the intensity upon applying flow varies monotonically between inlet and outlet. To the best of our knowledge, other spectroscopic flow experiments conducted so far only varied the flow rate in ranges where no dependency has been observed.^{10,21} Note that in Fig. 4.3a, we used is a 1 mM NaCl solution in pH 3 (HCl) with an additional 1 μ M NaF. The addition of a very low amount of NaF constrains the number of unknown parameters in our model. Fig. 4.3b compares experiments at the highest flow rate with and without the addition of 1 μ M NaF, from which it becomes clear that the added amount of sodium fluoride does not significantly influence the experimental results.



Fig. 4.2. Position and flow direction-dependent change in the v-SFG response upon flow. (a) Schematic representation of the flow setup. The aqueous solution reservoir (~100 mL of a 1 mM NaCl and HCl (pH 3) solution) is pumped via tubes and the flow cell using a peristaltic pump. The flow channel is 24.8 mm long, 4.3 mm deep, and 4.8 mm wide. The flow direction can be changed from clockwise to counter-clockwise. The v-SFG spectra were recorded at three spots in the channel. One spot in the center (yellow) and two points separated by 8 mm from the center in the two directions of the flow channel (blue and red, respectively). (b) Time trace of integrated SFG spectra (black circles) at the interface of the solution and fluorite for several flow-on/off cycles (black curve). As indicated by the arrows and the different signs of the flow rate, different flow directions were employed. The solid colored lines are ten-point averages to guide the eye highlight at which spot in the flow channel the spectra were recorded. For the time trace measured at the center, the intensity levels of the spectra with (I_{on}) and without flow (I_{off}) are highlighted by arrows.



Fig. 4.3. Gradient in the increase of the v-SFG intensity for different flow rates. (a) At different positions, the relative increase in the v-SFG intensity at the fluorite-water interface is calculated based on averaged steady state spectra under flow-on and flow-off conditions as marked in Fig. 3.4a and Fig. 4.1c for the three indicated flow rates. The open circles represent the relative increase upon flow and the filled symbols the mean at their corresponding positions. The error of the individual ratios (open circles) due to small fluctuations within the steady states of one flow-on/off cycle is negligible compared to the spread. The solid lines are guides to the eye. The solution used is a 1 mM NaCl solution in pH 3 HCl with an additional 1 μ M NaF. The addition of a very low NaF concentration constrains the number of unknown parameters in our model. The position is given as displacement from the center, with values increasing in the direction of flow, indicated by the arrow. **(b)** same as (a) for the highest flow rate only and comparing the solution with the added sodium fluoride with another one where no fluoride is added.

In summary, the v-SFG data reveal that flow triggers an increase of surface charge at every position in a channel. This increase varies monotonically along the channel length so that it is largest at the inlet and smallest at the outlet. This change in surface charge upon flow is reversible. Additionally, we found that the surface charge variation is also a function of the flow rate. To explain our observations quantitatively, we need a model that combines microscopic surface chemistry and macroscopic processes such as advection and diffusion in a flow system. This goes beyond the qualitative explanation by LIS et al.¹⁰. In the following section, we will introduce a self-consistent model that extends that of LIS et al.¹⁰ and describes not only the flow-dependent surface charge but also the dependency on flow rate and position.

4.3 Model of Surface Chemistry

First, we will briefly discuss the qualitative features of our model. We incorporate two reactions that take place at the fluorite-water interface (i.e., the wall of the flow channel): (i) The adsorption/desorption reaction of fluoride anions from equation (3.2), which determines the surface charge. In this reaction, only fluoride anions desorb from the surface to leave behind a positively charged $\equiv CaF^+$ unit on the surface, together with its back-reaction that involves F-adsorption. This reaction is responsible for the surface charging, and has been considered

responsible for the flow-induced change of the surface charge in previous work.¹⁰ However, as demonstrated below, a second reaction is necessary to explain the observations: (ii) The dissolution reaction of equation (3.13) in which a neutral CaF₂ unit dissolves from the surface in the form of three dissolved ions (one Ca²⁺ and two F⁻), together with its back-reaction, i.e., precipitation. This reaction is the source of fluoride anions without changing the surface charge.

Both reactions have a fluoride anion in common, which couples them. Fig. 4.4a illustrates this view of the surface chemistry. While LIS et al.¹⁰ and XI et al.²¹ only considered the adsorption/desorption reaction from equation (3.2) to qualitatively explain the flow-induced changes in the v-SFG spectra, we argue that a consistent and quantitative description of the experimental results also requires incorporating the dissolution as described by equation (3.13). The adsorption/desorption reaction of equation (3.2) alone could not serve as a steady state source for fluoride ions. During the continuous dilution with fresh solution from the reservoir in the flow-on period, the surface charge and thus the v-SFG signal would have to keep increasing, which is not observed experimentally as a steady state v-SFG signal is reached after 5 min. Therefore, our model considers the fluorite surface not only as an adsorption/desorption site for fluoride anions but also as an ion source for charge-neutral dissolution and precipitation of Ca²⁺ and two F⁻ according to equation (3.13). In fact, the dissolution reaction is not only a theoretical necessity but is also supported by the presence of calcium cations in flow experiments with fluorite.¹⁰

The appearance of a surface charge gradient upon flow can be explained when considering a flow-induced gradient in fluoride concentration along the mineral surface, as illustrated in Fig. 4.4 b. This gradient forms when the laminar flow transports dissolved fluoride anions along the interface, which leads to a build-up of fluoride ions at the outlet and a positive gradient in fluoride concentration in the flow direction. Moreover, because the solution flowing into the channel from the reservoir has a lower fluoride concentration, the fluoride ions are also diluted by the fresh solution, the more so the closer to the inlet. Thus, flow reversibly lowers the fluoride concentration everywhere in the channel, yet more so closer to the inlet. As the surface charge increases with lower fluoride concentration according to equation (3.2), the surface charge becomes larger at positions closer to the inlet. This qualitatively explains the gradient of the increase in surface charge along the surface upon flow and thus in the v-SFG response.



Fig. 4.4. **Model of Surface Chemistry along the flow channel. (a)** Illustration of the two interfacial reactions. Fluorite is not only an adsorption/desorption site for fluoride anions (equation (3.2)), which alters the surface charge, but also experiences charge-neutral dissolution-precipitation processes (equation (3.13)). The shared fluoride anion couples the two reactions. **(b)** Illustration of the flow channel. Without flow (upper part), dissolution creates an enhanced fluoride concentration in steady state, constant over the dissolving mineral surface, if the concentration reaches the saturation concentration. Dissolution rates and surface charge are also homogeneous along the mineral's surface. However, upon flow (lower panel), the concentration is lowered everywhere in the channel, the more so closer to the inlet. This leads to an increase in the surface charge and higher net dissolution than in flow-off conditions, both becoming smaller at the outlet.

The introduced model is used to perform numerical simulations. The description of the simulated flow setup and further details on the simulations have been described in section 3.4.2. The simulation leads to concentration profiles as visualized in Fig. 4.5. Fig. 4.5a shows the simulated flow setup under flow-off conditions, and Fig. 4.5b shows only the flow channel under flow-off and -on conditions in the upper and lower part, respectively. As explained in section 3.4.2, the origin of the coordinate system is located in the center of the flow channel. The flow channel has a radius of 2.4 mm and runs from $x = -L_{\rm C}$ to $x = +L_{\rm C}$ with $L_{\rm C} = 20$ mm. The dissolving mineral is located between $x = -L_S$ and $x = +L_S$ with $L_S = 12.4$ mm. The flow channel connects two reservoirs with fluoride bulk concentration $c_{F,b} = 1 \mu M$. Under flow-off conditions, the fluoride concentration in the flow channel reaches the saturation concentration of $c_{\text{F,sat}} = 10 \cdot c_{\text{F,b}} = 10 \,\mu\text{M}$. The simulated concentration profile upon flow in the lower part of Fig. 4.5b confirms the qualitative hypothesis of a concentration gradient along the mineral's surface within a layer of significantly higher concentrations. This result is consistent with our qualitative explanation of a concentration gradient for a surface charge gradient and the corresponding flow-induced gradient in the v-SFG intensity increase. The thickness of this layer, where the gradient occurs, is connected to the flow rate, as shown in Fig. 4.5c. At a flow rate of 1 mL·min⁻¹ we find that the typical layer thickness at which the radial concentration has decayed by 90% of its surface value is approximately 0.4 mm. This is still much thicker than the probing depth of our spectroscopic experiments.



Fig. 4.5. **Simulation of the flow channel and radial concentration profile. (a)** Illustration of the flow channel as used for the numerical calculations in COMSOL with resulting concentration profiles under flow-off condition. The center of the flow channel is at the origin (x = 0, r = 0). The channel length and diameter are $2 \cdot L_{\rm C} = 40$ mm and $2 \cdot R = 4.8$ mm, respectively, and the dissolving surface length is $2 \cdot L_{\rm S} = 24.8$ mm. The color represents the fluoride concentration with $c_{\rm F,b} = 1 \,\mu$ M as bulk concentration and $c_{\rm F,sat} = 10 \cdot c_{\rm F,b} = 10 \,\mu$ M as saturation concentration. **(b)** Zoom in on the channel under flow-off conditions (top) and flow-on conditions (bottom) at 1 mL·min⁻¹ in the positive *x*-direction as also indicated by the parabolic Poiseuille flow profile (white arrows). With flow, the concentration in the center of the channel essentially equals that in the reservoir. Nonetheless, a significant layer remains at the dissolving surface that exhibits a concentration gradient along the flow direction. **(c)** Radial concentration profiles of fluoride ions in the center of the channel at different flow speeds are shown based on the numeric simulations.

4.4 Lateral Concentration, Surface Charge, and Dissolution Profiles

From the numerical simulation of the concentration profiles, we can extract the concentrations at the interface. From those concentrations, the dissolution flux can be calculated based on equation (3.14), and the surface charge can be obtained from the adsorption/desorption reaction of fluoride from equation (3.2), incorporated via a Langmuir model as described in section 3.4.1. In the following, the concentration, surface charge, and dissolution profiles as well as how they describe the experimental v-SFG intensity changes along the mineral's surface, are discussed quantitatively. The profiles are shown in Fig. 4.6.



Fig. 4.6. Lateral gradients from the numerical model. (a) Calculated (lines) and experimentally obtained (symbols) relative changes in the v-SFG intensity along the mineral surface for different flow rates. For clarity, we show only the averaged values from Fig. 4.3 without the spread of the individual data points. (b) Calculated surface charge along the mineral surface for different flow rates, showing enhancements under flow-on conditions by approximately 50% compared to flow-off conditions. (c) Calculated fluoride concentration at the surface $c_F(x, R)$ relative to the bulk along the mineral surface for several flow rates. (d) The calculated net dissolution rate J(x) along the mineral surface for different flow rates. Note the orders of magnitude increase upon turning on the flow. Under flow-off conditions, the dissolution rate is a small fraction of the maximum dissolution rate $J \approx 10^{-5} k_{dis}$ while during flow the net dissolution increases by several orders of magnitude, to approximately half the maximal dissolution rate $J \approx k_{dis}$. The position is given as displacement from the center with values increasing in the direction of flow, indicated by the arrow in panel (c).

Fig. 4.6a shows the comparison between the experimentally observed changes in v-SFG intensity as a function of flow rate and position and those found in our numerical calculations (in which we tune the pressure drop to fit the experimental flow rate). The overall increase in the v-SFG response with increasing flow rate and its decrease from the inlet to the outlet is very similar to the surface charge characteristics (Fig. 4.6b). The surface charge increases by 50-100% compared to flow-off conditions, and varies by 10-20% laterally. The corresponding change in the surface potential Φ_0 (as calculated by the Gouy-Chapman relation in equation

(2.6)) is significantly lower in this nonlinear screening regime where Φ_0 exceeds the thermal voltage of 25mV, differing by only around 20% between the flow-on and flow-off states. Finally, to estimate the change in the SFG intensity, we use the approximation $(I_{\rm On} - I_{\rm Off})/I_{\rm Off} = (\Phi_{0,\rm On}/\Phi_{0,\rm Off})^2 - 1$ based on equation (2.40).

The calculated interfacial fluoride concentration (shown relative to the bulk concentration in Fig. 4.6c) decreases with increasing flow rate and increases from inlet to outlet. The reverse relation between fluoride concentration and surface charge stems from the Langmuir isotherm (equation (3.5)). Interestingly, although the fluoride concentration increases in the flow direction, Fig. 4.6c shows that the flow-induced dilution ensures that the concentration is lower throughout the channel than in the flow-off state. The concentration at the boundary of the dissolving area, at $x = -L_S$, is equal to the bulk concentration $c_{F,b}$ in flow-on conditions, beyond which it rises rapidly and then slowly reaches a maximum at $x = L_S$. This rapid increase of the fluoride concentration at $x = -L_S$ is due to the locally low precipitation rate at low fluoride concentrations compared to upstream locations near $x = L_S$.

In the flow-off state, the fluoride concentration in the center corresponds to the saturation concentration $c_{\text{F,sat}} = 10 \cdot c_{\text{F,b}}$. Without a precipitation reaction, the concentration would even be orders of magnitude larger. In our calculations that describe the experiment, the flow-induced change in fluoride concentration is in the order of ~30% of the saturation concentration ($c_{\text{F,sat}} = 10 \,\mu\text{M}$), as is evident from Fig. 4.6c. In an absolute sense, this change of concentration is orders of magnitude lower than the background ionic strength (~2 mM). While the change in fluoride concentration is sufficient to affect the surface charge, it is negligible for the total ionic strength that governs the screening of the surface charge. Thus, we can conclude from our combined experiments and theory that our flow-induced changes in the v-SFG signal are connected to the surface charge itself rather than changes in charge screening.

Finally, we draw attention to Fig. 4.6d, which reveals that the net dissolution rate also exhibits a gradient along the mineral surface and increases with flow rate. Similar to the position- and flow-rate-dependent shift in surface charge, the position-dependent net dissolution rate is also a result of the heterogeneous concentration profile. More importantly, however, we can see that the dissolution rate increases by orders of magnitude from flow-off to flow-on conditions. In the flow-off state, the surface concentration is nearly equal to the saturation concentration $c_F(x, R) \approx c_{F,sat}$, which causes the net dissolution rate in flow-off conditions to be ~10⁵ times smaller at the center than the maximum dissolution rate $2k_{dis}$. During flow the dissolution is almost as large as k_{dis} . The net dissolution rate thus increases by ~5 orders of magnitude due to flows of 1-6 mL·min⁻¹ (or shear rates of 1.5-9 s⁻¹), from effectively 10^{-7} to $10^{-2} \mu m^{-2} \cdot s^{-1}$.

4.5 Breakdown of Surface Charge Gradient

Under certain conditions, the flow-induced surface charge gradient can be expected to break down. Those conditions are very low flow rates, very high flow rates, and the prevention of a concentration difference between the reservoir and the flow channel by high fluoride bulk concentrations.

The limit of low flow rates is the flow-off state. As shown in Fig. 4.6, the profiles of interfacial fluoride concentration, surface charge, and dissolution rate are uniform along the mineral's surface under flow-off conditions. Certainly, a finite flow rate different leads to a dilution of the solution in the flow channel. However, for low flow rates, the dilution is small, and the change in the concentration profile can likewise be expected to be small, particularly close to the interface where the flow velocity is dramatically decreased due to the Poiseuille profile.

The other extreme regarding flow rates is the limit of very high flow rates. At such conditions, the concentration can also be expected to be uniform. Within this limit, the change of the flow rate does also not affect the magnitude of the flow-induced change. This explains why earlier studies^{10,21} did not observe a flow-rate dependency. Within this thesis, we come back to this limit in chapter 7.

Finally, high reservoir concentrations of fluoride anions lead to a breakdown of the gradient. If the solution from the reservoir, which is supposed to dilute the saturated solution within the flow channel, has a concentration comparable to that in the flow channel, the concentration profile will not be changed. This is why already LIS et al.¹⁰ observed no more change in the v-SFG intensity when several mM sodium fluoride was added to the solution. If the concentrations in the reservoir and the flow channel at flow-off conditions are identical, this means that at the mineral surface, dissolution and precipitation are balanced, i.e., no net-dissolution is happening. We reproduce this behavior and show that under such conditions, the gradient does indeed vanish as well as shown in Fig. 4.7a and b, respectively.



Fig. 4.7. Experimental results at high fluoride concentrations. (a) Exemplary time traces of the v-SFG intensity with two flow-on/off cycles (black curve) when using a 4 mM NaF solution in pH 3 HCl. Each open black circle stems from one integrated spectrum. The solid green line is a ten-point average to guide the eye (b) At different positions, the relative increase in the v-SFG intensity at the fluorite-water interface is calculated based on averaged steady state spectra under flow-on and flow-off conditions as marked in Fig. 3.4a and Fig. 4.1b. The open green circles represent these ratios and the filled symbols are the mean of the ratios at the corresponding positions. The flow rate was 6mL·min⁻¹. The solid line is a guide to the eye. The position is given as displacement from the center, with values increasing in the direction of flow, indicated by the arrow.

4.6 Transferability to Other Interfaces

Our theoretical model and v-SFG experiments can be transferred to other interfaces to determine the adsorption/desorption reaction mechanism and dissolution reaction mechanism. In the present case of calcium fluoride, the surface adsorption/desorption reaction (equation (3.2)) is desorptive, which implies that a decrease in the fluoride concentration increases the surface charge. Meanwhile, the dissolution reaction (equation (3.13)) is a source of reactive ions and hence increases the fluoride concentration. As flow brings the concentration closer to the reservoir's bulk concentration, the surface charge increases, more so at the inlet than at the outlet. The sign of the charges (i.e., whether an anion or cation is released) does not play a role in the surface charge's flow dependency. Interestingly, the combination of the surface being charged by desorption and dissolution being a source of ions partaking in this adsorption/desorption reaction is only one of several ways to establish a flow-dependent surface charge. For instance, a precipitating surface in contact with an oversaturated solution is a sink for the reactive ions. In this case, the concentration would increase upon flow, which for a desorptive charging mechanism would lead to a decrease, rather than an increase, in surface charge. This decrease is higher the closer to the inlet. Another charging mechanism is the adsorption of a reactive ion, where the surface charge increases with increasing concentration of reactive ions. This causes the surface charge to increase upon flow when the surface is a sink

and to decrease upon flow when the surface is a source of reactive ions. Note that whether the surface is a sink or a source of ions is not necessarily determined by whether the mineral is dissolving or precipitating. For instance, protons play a role in the charging of iron oxide surfaces and are consumed when iron oxide dissolves.¹²⁰ In this case, the surface is a sink below the saturation concentration and a source above saturation concentration. As protons are often consumed in dissolution and partake in the charging of metal oxides, we expect such counter-intuitive behavior to be relatively common.

We summarize the expected change in surface charge upon flow for different combinations of charging and dissolution reactions in Fig. 4.8. If either the dissolution or adsorption/desorption reaction is known, the other reaction mechanism can be established by inspecting the sign of the v-SFG change upon flow or the slope of the flow-induced surface charge gradient. This could be useful for the investigation of other minerals, for instance, the notoriously complex surface chemistry of silica.^{116,121-125}

Charging is Surface is	Desorptive	Adsorptive
Source	仑	₽ ₽
Sink	$\overline{\nabla}$	仑

Fig. 4.8. Overview of charging and dissolution coupling. Indication whether the surface charge increases (arrow up) or decreases (arrow down) upon flow. The column position indicates if the surface is a source or sink of reactive ions, the row position indicates if the reactive ion desorbs or adsorbs to generate surface charge. The change of surface charge upon flow is always larger at the inlet than at the outlet.

4.7 Conclusion

In conclusion, we demonstrated that the surface charge and dissolution rate of calcium fluoride show macroscopic gradients along the interface when flow is applied. This was shown by the combined use of surface-specific v-SFG spectroscopy and full numerical calculations of reaction-diffusion-advection equations, including the interfacial chemistry at mineral-water interfaces. We extended v-SFG spectroscopy spatially to investigate the surface chemistry of fluorite upon flow on a macroscopic scale. The observed gradient in the v-SFG response can be correlated to a gradient in the surface charge upon flow. A dissolution-diffusion-advection process can entirely explain such a gradient. The key physicochemical mechanism is captured by the coupling of a dissolution reaction with flow and surface charge. This dissolution reaction creates a steady state concentration profile of fluoride ions, which depends on both position and flow rate. Both the surface charge and dissolution rate are influenced by the local fluoride concentration. Thus, dissolution also causes a position-dependent dissolution rate and surface charge upon flow. Our reaction-diffusion-advection model can be generalized to arbitrary surface and dissolution reactions. We expect that the method of position resolved v-SFG spectroscopy can be transferred to other systems to determine charging and dissolution mechanisms. Interfaces exhibiting both dissolution and charging in flowing water occur naturally in a wide variety of systems. Thus, our finding of a flow-induced gradient in the dissolution reaction is expected to impact geological research. Also, scientific disciplines that rely on the use of surface potentials, such as electrokinetics, microfluidics, and nanofluidics, or those involving measurements of surface potentials, may be interested in its dependency on the position and flow rate.

5 Studying the Interplay of Fluoride and Calcium Adsorption/Desorption

While the previous chapter provided an improved understanding of the flow-induced effects, particularly, at the fluorite-water interface, a general question on the underlying model can be raised: Does calcium adsorption/desorption also contribute to the surface? This question is addressed in the present chapter, which is part of a manuscript that is currently in preparation under the working title "Flow experiments reveal the interplay of different adsorption reactions at a mineral-water interface".

The interaction of fluoride and calcium ions with the charged fluorite surface reflects a controversy in the literature. While ζ -potential measurements by MILLER et al.¹²⁶ assigned a potential determining role to calcium ions, more recent studies of KHATIB et al.¹⁵ and LIS et al.¹⁰ explain the positive surface charge in terms of fluoride vacancies. The latter consideration has also been the fundament of the fluoride adsorption/desorption model discussed in the previous chapter. Since the fluoride adsorption/desorption model can explain the previous observations, this process would clearly be dominant compared to a surface reactions that involves calcium ions. However, the question on the role of calcium remains. We therefore desire to systematically suppress the dominant fluoride adsorption/desorption reaction in this chapter in order to look for a potential calcium adsorption/desorption reaction.

5.1 Variation of Fluoride Concentration

We performed experiments with and without applied flow at the fluorite-water interface under acidic conditions (HCl solution at pH 3). We systematically varied the fluoride bulk concentration by adding different amounts of sodium fluoride to the pH 3 solution. Under acidic conditions, the adsorption/desorption of fluoride has already been connected to the surface charge in the previous chapter and in literature.^{10,15,18} Therefore, we chose those conditions to suppress the influence of fluoride adsorption/desorption in order to look for a contribution of calcium adsorption/desorption.

A selection of v-SFG spectra for different fluoride bulk concentrations is shown in Fig. 5.1a. From those spectra, it is clear that the increase in fluoride bulk concentration decreases the magnitude of the v-SFG intensity dramatically. To quantify this decrease, we plotted the integral of the spectra as a function of the added sodium fluoride in Fig. 5.1b. Every filled black circle represents one integrated spectrum. The integrated values are normalized to the value obtained with the bare pH 3 solution, which also enables a day-to-day comparability of the intensities. The v-SFG intensity decreases monotonically with the addition of fluoride. This decrease is steeper at lower fluoride concentrations, like 20% between 1 and 10 μ M compared to 6% between 1 and 3 mM. In fact, the intensity seems to level off at mM fluoride concentrations. For the highest fluoride bulk concentration investigated, the intensity drops to $\sim 15\%$ of the intensity without added fluoride (bare pH 3). According to equations (2.6) and (2.40) such a decrease in v-SFG intensity can be assigned to a lower surface potential as a result of either increasing ionic strengths and/or decreasing surface charges. In the experiments, both are occurring. However, the increase in ionic strength is minor, because all solutions are based on pH 3 and thereby have already an ionic strength in the mM range. Additionally, the most pronounced changes in the v-SFG intensity occur up to 0.1 mM added sodium fluoride where there is hardly a change in the ionic strength. Therefore, the decrease in surface charge can be considered dominant for our observations. The connection between surface charge and fluoride concentration can be explained by equation (3.2). With higher fluoride bulk concentrations, the adsorption/desorption equilibrium is shifted to the left-hand side (adsorption), resulting in lower surface charges. This leads to a decrease in the net orientation and polarization of the probed water molecules as illustrated in the inset of Fig. 5.1b. This lower net-orientation and a lower degree of polarization are the reasons for the v-SFG intensity to decline. Consequently, the presented dependency of the v-SFG intensity on the fluoride concentration is consistent with earlier spectroscopic studies and their conclusion that adsorption/desorption of fluoride anions affects the surface charge and potential. 10,15,21



Fig. 5.1. Fluoride concentration-dependent results in flow-off and flow-on experiments. (a) V-SFG spectra of the fluorite-water interface in the absence of flow with increasing fluoride bulk concentration. The spectra were recorded in total internal reflection geometry and are not normalized to the IR shape. Such normalization is not necessary to investigate the change in v-SFG intensity and surface charge for different fluoride bulk concentrations. (b) Dependency of the v-SFG intensity on the amount of added sodium fluoride. The experimental values (filled black circles) arise from integrating the spectra. The data points are normalized to the bare pH 3 solution, with no fluoride added to the bulk solution. Inset is an illustration of the decreasing surface charge as the cause for less netorientation of the interfacial water molecules resulting in the decreasing v-SFG intensity. The integrals corresponding to the spectra from Fig. 5.1a are marked by a colored circle with the color matching to the spectra shown in panel (a). (c) V-SFG intensity development during a flow-on/off cycle (solid black line in bottom panel). Each open black circle represents one integrated spectrum. The solid colored lines are ten-point moving averages to guide the eye and refer to the concentration from Fig. 5.1a and b at which the flow experiment is conducted. In the top trace, the level of the v-SFG intensity at flow-on and flow-off conditions is marked by arrows with *I*_{on} and *I*_{off}, respectively.

In chapter 4 and in literature^{10,21}, it has been shown that upon flow adsorption/desorption equilibria are altered. In the case of calcium fluoride, a flow-induced increase in surface charge has been observed and was explained by a dilution in the fluoride concentration shifting the adsorption/desorption equilibrium of fluoride to the right-hand side of equation (3.2). With the addition of fluoride, we aim to suppress the alteration of the fluoride adsorption/desorption equilibrium. Such an experiment has the potential to reveal weaker contributions to the surface charge, like a calcium adsorption/desorption reaction. A selection of the experimental results for some fluoride bulk concentrations is shown in Fig. 5.1b, where the color of the solid line (a moving average) matches with the color highlighting the concentration in Fig. 5.1a and b. Each open circle in Fig. 5.1b represents one integrated spectrum. The applied flow rate was 6 mL·min⁻¹ ($Re\approx$ 24). It becomes clear that the presence of flow changes the v-SFG intensity. This change depends on the fluoride bulk concentration. In chapter 4, we have shown that the

application of flow dilutes the solution inside the flow channel with respect to the bulk concentration in the reservoir. Inside the flow channel, we can assume saturated concentrations due to the dissolution of the mineral. The degree of dilution depends on the provided difference in bulk concentration and the saturation concentration. While the v-SFG intensity increases upon flow at low fluoride bulk concentrations (e.g., bare pH 3 solution, red line in Fig. 5.1b), the intensity stays constant at high fluoride concentrations (e.g. addition of 3 mM NaF, blue line in Fig. 5.1b). Those observations are consistent with the discussion in chapter 4 as well as previous studies.^{10,21} At low fluoride bulk concentrations, the chemical equilibrium in the adsorption/desorption reaction from equation (3.2) is shifted to the right-hand side with the higher surface charge due to the decrease in fluoride concentration upon flow-induced dilution. In contrast, at high fluoride concentrations, the change in concentration upon flow will be minor. Consequently, the surface charge does not change significantly. Interestingly, we observe for intermediate fluoride bulk concentrations around 1 mM added sodium fluoride (green line in Fig. 5.1b), that the v-SFG intensity decreases upon flow. Note that we have observed more pronounced decreases as shown in Fig. 5.2a, which emphasizes the significance of the underlying process. It is worth mentioning that the experimental data shown in Fig. 5.2a was not obtained as part of a series of measurements in which the concentration was varied (as reported in Fig. 5.1c). The different magnitude of responses reported in Fig. 5.1c and Fig. 5.2a indicates a memory effect. It is perhaps not surprising that the details of the reactivity of the surface depends on its history.

5.2 Confirming Calcium Adsorption/Desorption

As discussed earlier, the v-SFG intensity can be used as a measure for the surface charge. Based on the observed decrease in the v-SFG intensity upon flow at 1 mM fluoride bulk concentration, the question arises, which process may lead to a flow-induced surface charge decrease at this fluoride bulk concentration. One explanation could be that flow actually increases the local fluoride concentration, if the solution is already oversaturated and precipitation occurs at the surface, decreasing the local fluoride concentration at flow-off conditions. This corresponds to the surface being a sink of the reactive ion (see section 4.6). Another explanation is that at 1 mM added fluoride, calcium adsorption/desorption becomes dominant over the fluoride adsorption/desorption. In this case, flow-induced dilution of calcium favors its desorption and thereby decreases the surface charge, which is observed by the falling v-SFG signal.



Fig. 5.2. Calcium adsorption/desorption determines the flow-induced change in v-SFG intensity at 1 mM added NaF. V-SFG intensity development during a flow-on/off cycle (solid black line in bottom panel). Each open black circle represents one integrated spectrum. The colored solid lines are ten-point moving averages to guide the eye. **(a)** The decrease in v-SFG intensity upon flow for a pH 3 solution with 1 mM NaF added to that solution is here approximately twice that presented in Fig. 5.1c. While this higher magnitude of the intensity decrease upon flow stretches the significance of the underlying process, it raises the question of why the magnitude varies so much. In this particular experiment, it was not a series of concentrations that was investigated. Despite possible variation in reactivity of the surface, this could be an indication of a memory effect. As it is the aim of this chapter to discuss the interplay of adsorption/desorption reactions, we quantify only the several times measured series of concentrations. **(b)** The top panel shows the intensities of the same flow experiment conducted with a 1 mM NaF pH 3 (HCl) solution, and the middle panel shows the data for the same solution that additionally contains 10 μM CaCl₂. The v-SFG intensities under flow-off conditions are normalized as in Fig. 5.1a. We switched two times between the two solutions and observed the same behavior for absence and presence of calcium.

To discriminate between the two possible explanations, we performed experiments with added calcium, because the observed decrease in the v-SFG intensity upon flow is expected to change differently according to the two proposed explanations. In the case of precipitation during flow-off conditions, an increased bulk calcium concentration makes the solution being more oversaturated and, therefore, enhances precipitation. Thus, the flow-induced decreases in surface charge and v-SFG intensity will be more pronounced. In contrast, if the observed decrease in the v-SFG intensity upon flow is due to a dilution in calcium concentration indicating calcium adsorption/desorption, adding calcium to the bulk will lower the dilution upon flow. Consequently, the change in surface charge and the corresponding v-SFG intensity will be less pronounced when calcium is added to the bulk. Fig. 5.2 shows the results of such flow experiments with 1 mM NaF pH 3 (HCl) solutions with and without the addition of 10 µM CaCl₂. Adding those $10 \,\mu\text{M}$ CaCl₂ changes the ionic strength only by ~2%, which is negligible. Therefore, any observed differences between the solutions are due to the introduction of Ca²⁺ in the reservoir. Clearly, the flow-induced change in the v-SFG intensity becomes smaller when $10 \,\mu\text{M}$ CaCl₂ is added. We switched twice between the two solutions and observed the same behavior for the absence and presence of calcium. This reproducible effect of the presence of calcium on the flow-induced decrease in the the v-SFG intensity upon flow is consistent with

calcium adsorption/desorption but not a precipitation process. We can thus conclude that both fluoride and calcium adsorption/desorption competitively contribute to the surface charge. Upon flow, the two reactions have opposite effects: While a dilution in the fluoride concentration increases the surface charge (i.e., driving the equilibrium from equation (3.2) to the right-hand side), a dilution in calcium concentration decreases the surface charge (i.e., driving the equilibrium from equation (3.6) to the left-hand side). At 1 mM fluoride bulk concentration, we suppressed the effect of fluoride adsorption/desorption on the dilution upon flow, revealing the calcium contribution. Since the addition of fluoride suppresses also the dissolution process, also the calcium dilution becomes smaller with increasing fluoride concentrations, which is why, at 3 mM of added sodium fluoride, there is no more change upon flow.

The validity of calcium adsorption/desorption is further supported by the magnitude of the v-SFG intensity in the flow-off state. From comparing the two data sets in Fig. 5.2, it is clear that the addition of calcium increases the surface charge as one can see from the 10% higher v-SFG intensity in flow-off condition. This increase in surface charge upon added calcium is consistent with adsorption of calcium increasing the surface charge as in equation (3.6). Finally, we learn from the data in Fig. 5.2 that the mixture of 1 mM fluoride and 10 μ M calcium is close to but still below the saturation condition as only a small but noticeable flow effect is observed. The concentration product under these conditions is 10^{-11} M³, which is close to the literature value of $3.45 \cdot 10^{-11}$ M³.¹¹² Consequently, the combination of surface-sensitive v-SFG spectroscopy and flow experiments does not only reveal the interplay of fluoride and calcium adsorption/desorption reactions but is also suitable to determine the solubility product of fluorite. The entirety of information accessible via our experiment shows its significance for studying interfacial chemistry.

5.3 Comparing Fluoride and Calcium Adsorption/Desorption

Based on the evidence for an interplay of fluoride and calcium adsorption/desorption at the fluorite-water interface, we would like to compare and quantify the contributions of those two reactions. Clearly, the fluoride adsorption/desorption reaction is dominant, which causes the increases in the surface charge and v-SFG intensity upon flow when no fluoride is added. This dominance is consistent with an electrostatic perspective. Since the fluorite surface is positively

charged under the investigated conditions, fluoride adsorption is favored versus calcium adsorption. To estimate the ratio between fluoride and calcium adsorption/desorption rates, we fit the experimental data with a model based on the two adsorption/desorption reactions and the dissolution process. We fitted the normalized v-SFG intensities from Fig. 5.1b and their flowinduced change. The latter is quantified as the relative increase of the v-SFG intensity upon flow, $(I_{\rm on} - I_{\rm off})/I_{\rm off}$, as intensity levels introduced in Fig. 5.1c. Note that we only included data of experiments where we have investigated a series of concentrations. The experimental data (filled circles) and our fit (solid orange lines) are shown in Fig. 5.3a and b. To obtain those curves, the adsorption/desorption equilibria for fluoride and calcium, which determine the surface charge, are incorporated via a simple Langmuir model (see chapter 3.4.1 for details). This model requires knowledge of the concentration of the adsorbing/desorbing ions. While the flow-off conditions can be described by assuming saturation concentrations due to dissolution of fluorite, the flow-on concentrations need to be between the flow-off concentrations and the bulk concentrations because the presence of flow dilutes the solution in the flow channel with the bulk solution from the reservoir. Thus, the flow condition is incorporated by an effective dilution of 35%, which is comparable to the result from the simulations of the previous chapter. Furthermore, the fluoride bulk concentration can not simply be described by the amount of added fluoride but needs to be corrected for the formation of HF. This process is also increasing the pH. We have measured a pH increase of ~ 0.5 units with the highest fluoride concentration used here, which is consistent with what one would expect based on the pK_a of 3.2.¹¹² Since a higher pH is known to decrease the v-SFG intensity¹⁰ like the reduced surface charge due to fluoride adsorption, we measured the v-SFG as a function of pH (Fig. 5.3c). The dependency of the v-SFG intensity on the pH is fitted linearly (solid black line in Fig. 5.3c) and incorporated in the modeling as a phenomenological correction factor. Further details on the modeling can be found in section 3.4.3.



Fig. 5.3. Modeling of experimental data. (a) V-SFG intensity as a function of added sodium fluoride as in Fig. 5.1b. The solid orange line is based on our model with the parameters chosen as the best description. **(b)** Plot of the relative change in the v-SFG intensity induced by flow as a function of the added sodium fluoride. The filled circles represent the experimental values obtained from the flow cycles. The solid orange line corresponds to the parameters we have chosen as the best description. **(c)** V-SFG intensity as a function of pH. The pH is set by diluting a hydrochloric acid (HCl) solution. The values are based on three independent series where the solutions were measured in the order of increasing pH at least two times in a row. For one series, the data point for the pH 3 solution was missing, so the series is normalized to the pH 3.1 intensity of the first round. The solid black line is a linear fit, which, normalized to pH 3, is used as a correction to incorporate the pH dependency in our modeling.

As described in sections 3.4.1 and 3.4.3, the chosen parameters for our model leading to the orange fit are $\Gamma = 10^{-19} \text{ m}^{-2}$, $L_{\text{CaF}_2} = 3.45 \cdot 10^{-2} \text{ mol}^3 \cdot \text{m}^{-9}$, and 35% dilution upon flow. The parameters $\chi^{(3)'}/\chi^{(2)} = 250 \text{ V}^{-1}$ and the ratio of the rate constants $k_{ads,F}/k_{des,F} = 700 \text{ m}^3 \cdot \text{mol}^{-1}$ for fluoride and $k_{ads,Ca}/k_{des,Ca} = 0.005 \text{ m}^3 \cdot \text{mol}^{-1}$ for calcium adsorption/desorption were chosen to fit the experimental data and to match the surface potential at zero added sodium fluoride with the reported zeta potential of ~70 mV.^{13} The absolute $\chi^{(3)'}/\chi^{(2)}$ ratio is high compared to those known for the silica-water interface, suggesting a dominance of the $\chi^{(3)}$ -contribution. Despite its conceptual simplicity, our model captures the main behavior of the experimental data as shown in Fig. 5.3a and b. This behavior is the monotonic decrease in the v-SFG intensities with increasing fluoride concentration under flow-off conditions and the transition from a flow-induced increase in the v-SFG intensity at low fluoride concentrations to a flow-induced decrease at intermediate concentrations, which approaches zero with a further increase in concentration. However, the model misses the steep decrease at low fluoride concentrations and underestimates the plateau level in the mM range for the flow-off intensities. Additionally, the model shows a shifted and stretched curve of the flow-induced
changes. Roughly, the experimental data exhibits a fluoride concentration dependence that differs from the model by about a factor of two.

These deviations can be, at least partly, understood from the limitations of our model. Important simplifications are the assumptions underlying the used Langmuir model, like a homogenous surface and the independence of the adsorption processes, which particularly means that we neglect electrostatic interactions between fluoride ions and the positively charged surface. There are likely sites of higher and sites of lower reactivity. Moreover, fluoride adsorption should become less likely with higher fluoride concentrations due to a less positive surface charge upon adsorption. Conceptually, those two effects should shift our fits to lower concentrations. Additionally, our model is based on a charge-independent $\chi^{(2)}$ and the Gouv-Chapman model, which is known to break down at higher surface potentials. As we assign all changes in the v-SFG intensity to changes in the surface potential within the Gouy-Chapman model, we also overestimate the potential decrease upon fluoride addition down to 9 mV.¹³ Despite these approximations, our model reasonably describes the observed trends in the v-SFG experiments and is conceptually simple with few free parameters. The density of surface sites is reasonable, given the crystal structure, the HF formation is based on the pK_a from literature, the effective dilution is taken from simulations, and the combination of rate constants is chosen to match zeta potentials from literature at pH 3.

We want to emphasize that the purpose of the modeling is to estimate the ratio between fluoride and calcium adsorption/desorption. From our model, the adsorption/desorption ratio of fluoride is about five orders of magnitude higher than the one of calcium. To confirm this dominance, we discuss next how a comparably slight variation in those ratios by a factor of five affects the quality of the fit and the description of the surface potential at zero added fluoride. Fig. 5.4 and Table 5.1 show how varying those parameters affect the fits and the surface potential. For the fitting, we treat the inverse of the $\chi^{(3)'}/\chi^{(2)}$ ratio as fit parameter. A value of infinity for this parameter, as represented by the dark blue line, corresponds to the best fit having zero $\chi^{(2)}$ -contribution.

If we consider, for instance, the steepness at low fluoride concentrations and the plateau at high fluoride concentrations within the flow-off intensities, an increased fluoride adsorption rate (light blue curve in Fig. 5.4a) improves the description of the experimental data compared to our selected parameter combination (orange line). However, such a higher fluoride adsorption/desorption ratio leads to lower surface potentials and thus misses the reported zeta potentials of 70 mV, as shown in Table 5.1. Additionally, with the increased fluoride adsorption/desorption ratio, the flow-induced changes can no longer be described sufficiently.

The first regime of a flow-induced increase in Fig. 5.4b is missing completely, and the flowinduced decreases are much more overestimated. A similar worsening appears when increasing the adsorption/desorption ratio of calcium (dark red line). In contrast, when decreasing the adsorption/desorption rates, the model hardly shows the regime of flow-induced decreases of the v-SFG intensity and overestimates the flow-induced increases massively (dark blue and light red line). One may also consider modifying both adsorption rates to obtain a better description. In fact, there is no combination that could improve the description of flow-off intensities, flowinduced changes, and surface potential. For instance, the decrease in the surface potential when increasing the fluoride adsorption/desorption rates could be compensated by increasing the calcium adsorption/desorption rate. However, both changes in the adsorption/desorption rates worsen the description of the flow-induced changes in the same manner (dark red and light blue lines in Fig. 5.4b).



Fig. 5.4. Influence of varying model parameters on the fits. (a) Experimental and fitted v-SFG intensity as a function of added sodium fluoride as in Fig. 5.3a but with additional fits where the ratios of the rate constants are varied according to Table 5.1. **(b)** Experimental and fitted relative changes in the v-SFG intensity induced by flow as a function of the added sodium fluoride as in Fig. 5.3b but with additional fits where the ratios of the rate constants are varied according to Table 5.1.

	Model	Model with 5 x F ⁻ adsorption	Model with 0.2 x F ⁻ adsorption	Model with 0.2 x Ca ²⁺ adsorption	Model with 5 x Ca ²⁺ adsorption
$\chi^{(3)'}/\chi^{(2)}$ (V-1)	250	63	00	28	51
$k_{ads,F}/k_{des,F}$ (m ³ ·mol ⁻¹)	700	3500	140	700	700
k _{ads,Ca} /k _{des,Ca} (m ³ ·mol ⁻¹)	0.005	0.005	0.005	0.001	0.025
Φ_0 (mV)	70	42	130	55	113

Table 5.1 Variation of model parameters. The variation of the ratio of rate constants of fluoride and calcium adsorption leads to different surface potentials and $\chi^{(3)'}/\chi^{(2)}$ values for fitting the data as in Fig. 5.3.

The purpose of the modeling is to estimate the ratio between the fluoride and calcium adsorption/desorption rates: With the used parameters, the ratio of the rate constants for fluoride and calcium adsorption/desorption differ by about five orders of magnitude. The variation in the parameters by a factor of only 5, changes the surface potential substantially and worsens the description of the flow-induced changes in the v-SFG intensity massively. Therefore, and given the simplicity of the model, we are confident in concluding from the modeling that the fluoride adsorption/desorption ratio is several orders of magnitude larger than the calcium adsorption/desorption ratio. This clear dominance makes it remarkable that the small contribution of calcium adsorption/desorption can determine the flow-induced changes at a certain fluoride bulk concentration. These observations highlight the high sensitivity of our experiments to different adsorption/desorption reactions. Clearly, one needs a very sensitive experimental approach, like the combination of surface-specific v-SFG spectroscopy and flow experiments, in order to uncover the complex interplay of such reactions.

5.4 Conclusion

This chapter demonstrates that the combination of surface-specific v-SFG spectroscopy and flow experiments is suitable to uncover the complex surface chemistry of adsorption/desorption reactions at the fluorite-water interface. Due to the high sensitivity of our approach, we revealed that calcium adsorption/desorption is a small contribution to the surface charge in addition to the dominant fluoride adsorption/desorption. Based on v-SFG experiments with and without applied flow for a series of fluoride concentrations, we suppressed the contribution of fluoride adsorption/desorption to the flow-induced alteration in the chemical equilibrium at the interface. We verified our hypothesis by comparing experiments at one fluoride concentration with and without the addition of only 1% calcium relative to fluoride. We also showed that our investigations are suitable for determining solubility products. Our interpretation is further supported by a simple model based on two competing Langmuir adsorption/desorption reactions, which allowed us to establish the dominance of the fluoride adsorption/desorption reaction. Overall, the combination of surface-specific v-SFG spectroscopy and flow experiments can be used to obtain a very detailed picture of the chemistry at a mineral-water interface. It is possible to reveal the interplay involving even very small contributions and thus the complexity of interfacial reactions. We, therefore, expect that this approach finds its application in future

investigations of surface reactions at a variety of solid-fluid interfaces, particularly in geochemistry.

6 Ion-specific Interactions at the Fluorite-Water Interface

In natural settings, a mineral faces a variety of different ions upon contact with water. The interactions between a mineral and the aqueous phase are often ion-specific.^{18,19,27,94} Therefore, the understanding and modelling of geochemical processes require studying those ion-specific effects. The common mineral fluorite has already been the objective of such studies.^{10,13,18,19,127}

In chapter 5, the combination of flow experiments and surface-sensitive v-SFG spectroscopy has been introduced as a sensitive tool to investigate different adsorption reactions at the fluorite-water interface. Based on that approach, the current chapter covers the investigation of ion-specific effects at the fluorite-water interface. This chapter is part of a manuscript that is currently in preparation under the working title "Studying ion-specific interactions at a mineral-water interface by surface-specific spectroscopy and flow experiments".

6.1 Overview

We investigated the fluorite-water interface for a selection of ions in an aqueous solution with and without the application of flow. The flow rate was 6 mL·min⁻¹ ($Re\approx24$). As in the previous chapters, all solutions are based on a pH 3 (HCl) solution to which different salts are added in order to study the ion-specific interaction with the charged fluorite surface. The investigated ions are alkali cations as well as the calcium and magnesium cation based on their chloride salts, and the halides fluoride to iodide as well as the sulfate anion based on their sodium salt. The results of our experiments for all the investigated salts are summarized in Fig. 6.1. Fig. 6.1.a shows the v-SFG intensity under flow-off conditions normalized to a bare pH 3 solution, and Fig. 6.1.b shows the relative changes in the v-SFG intensity upon flow $(I_{On} - I_{Off})/I_{Off}$. According to the flow-induced changes, we divide the ion-specific effects in three categories:

- 1. No change in the v-SFG intensity upon flow (sodium fluoride & calcium chloride).
- 2. Less increase in the v-SFG intensity upon flow (sodium chloride, lithium chloride, potassium chloride, cesium chloride & sodium bromide).

3. Decrease in the v-SFG intensity upon flow (sodium iodide, sodium sulfate, rubidium chloride & magnesium chloride).

Those three categories are discussed in the following sections of this chapter. The discussions will also consider the magnitude of the v-SFG intensity from Fig. 6.1.a.



Fig. 6.1. Ion-specific influence on the v-SFG intensity and its change upon flow. (a) Flow-off v-SFG intensities at the fluorite-water interface at pH 3 (HCl) with the addition of the listed ions. The added concentrations are $c_{\text{NaF}} = 100 \text{ mM}$, $c_{\text{CaCl}_2} = 50 \text{ mM}$, $c_{\text{NaCl}} = 100 \text{ mM}$, $c_{\text{LiCl}} = 100 \text{ mM}$, $c_{\text{KCl}} = 100 \text{ mM}$, $c_{\text{CsCl}} = 100 \text{ mM}$, $c_{\text{NaBr}} = 100 \text{ mM}$, $c_{\text{Na}} = 50 \text{ mM}$, $c_{\text{Na}} = 100 \text{ mM}$, and $c_{\text{MgCl}_2} = 50 \text{ mM}$. The intensities are normalized to the one obtained with a bare pH 3 (HCl) solution. The filled circles represent averages over several experiments while the open circles represent the spread of the single experiments. **(b)** Relative change in the v-SFG intensity upon flow at the fluorite-water interface with the same solutions as used in (a).

6.2 No Change upon Flow: Suppression of Dissolution

In the last two chapters, we have seen, that no more flow-induced change in the v-SFG intensity is observed at sufficient high fluoride bulk concentrations. This is now reproduced at even higher fluoride concentrations as shown in Fig. 6.1b and Fig. 6.2a. So far, we have explained the loss of a flow-induced change in the v-SFG intensity by suppression of dissolution. If dissolution is sufficiently suppressed, there is no more concentration difference between the reservoir and the flow channel where the mineral faces the solution and dissolves. Therefore, the application of flow does not lead to a change in concentration. Thus, the adsorption/desorption of ions does not change upon flow. Consequently, the surface charge and the corresponding v-SFG intensity is unaffected by flow. Additionally, the high fluoride bulk concentration shifts the adsorption/desorption equilibrium of fluoride anions from equation (3.2) to the uncharged left-hand side, which explains the low v-SFG intensity in Fig. 6.1a due to a low surface charge.



Fig. 6.2. Exemplary results of flow experiments with added NaF and CaCl₂. Integrals of v-SFG spectra as a function of time during one flow-on/off cycle. The fluorite prism is in contact with an aqueous solution based on a pH 3 (HCl) solution to which the indicated salts with the given concentrations are added. The intensities are normalized to bare pH 3 according to the average values from Fig. 6.1a. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panels shows the applied flow rate as a function of time.

Apart from an excess of fluoride anions, also a high calcium concentration can be expected to suppress dissolution. Accordingly, no flow-induced change in the v-SFG intensity should be present. We observe this expected behavior at 50 mM added calcium chloride (Fig. 6.2b). However, the magnitude of the v-SFG intensity is much higher when calcium is added compared to when fluoride is added (Fig. 6.1a). This can be explained by the absence of fluoride anions in the bulk solution, enhancing fluoride desorption. In fact, more desorption of fluoride ions and the presence of calcium ions might lead to the expectation of a surface charge that is even higher than the one at the bare pH 3 solution, because, according to chapter 5, calcium can adsorb at the fluorite surface. Accordingly, one might expect a higher v-SFG intensity with the calcium solution than with the bare pH 3 solution. However, Fig. 6.1a and Fig. 6.2b show that with the addition of 50 mM CaCl₂, the v-SFG intensity is ~80% of the one obtained with the bare pH 3 solution. Such a decrease in the v-SFG intensity might arise from the high ionic strength, which is almost 2 orders of magnitude higher than the bare pH 3 solution. This increase in ionic strength causes charge screening and reduces the surface potential, which determines the v-SFG intensity as in equation (2.40).

6.3 Less Increase upon Flow: Charge Screening

A decrease of the v-SFG intensity due to charge screening at increasing ionic strength has been discussed in previous studies.^{25,35,99} To discuss the influence of screening in the present case, we aim to compare first the results obtained by using a bare pH 3 solution with those obtained by adding sodium chloride to the solution. For sodium and chloride we do not expect other interactions with the fluorite surface different from charge screening.¹⁹ In fact, we have already assumed, without mentioning, that no other interactions are present for sodium and chloride when discussing the influence of fluoride and calcium. In those experiments also sodium and chloride, respectively, were present. The sodium chloride concentration used in the following experiment is the same as for the sodium fluoride solution from the previous section (100 mM), which gives an ionic strength that is also similar to that of the calcium chloride solution.

When using a bare pH 3 solution, a flow-induced increase by \sim 30% is observed, as shown in Fig. 6.3a. This increase is consistent with the discussions in the previous chapters. Briefly, this effect mainly arises from the flow-induced dilution in fluoride concentration, which shifts the adsorption/desorption equilibrium of fluoride anions from equation (3.2) to the right-hand side, increasing the surface charge and thus the measured v-SFG intensity. With the addition of sodium chloride, we observe a reduced v-SFG intensity and a lower increase upon flow (Fig. 6.1 and Fig. 6.3b).



Fig. 6.3. Exemplary results of flow experiments with bare pH 3 and added NaCl. Integrals of v-SFG spectra as a function of time during one flow-on/off cycle. The fluorite prism is in contact with an aqueous solution based on a pH 3 (HCl) solution to which 100 mM sodium chloride is added. The intensities are normalized to bare pH 3 according to the average value from Fig. 6.1a. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panels shows the applied flow rate as a function of time.

With the 100 mM sodium chloride solution, the v-SFG intensity is \sim 75% of that obtained with the bare pH 3 solution (Fig. 6.1a). Such an intensity decrease is consistent with previous studies.¹⁹ The v-SFG intensity is also close to the one obtained with 50 mM $CaCl_2$ solution (Fig. 6.1a), which suggests comparable surface potentials. Concerning the flow-on/off experiments in the presence of the sodium chloride, Fig. 6.3b shows that flow does still increase the v-SFG response. However, compared to the bare pH 3 solution, the addition of sodium chloride decreases the flow-induced change in the v-SFG intensity from +30% (bare pH 3 solution) to +5% (Fig. 6.1b). To understand this reduction, it is important to realize that we assume the v-SFG intensity to scale with $|\chi^{(2)} + \chi^{(3)'} \cdot \Phi_0|^2$ (see section 2.4.5). From these two terms, the first term $(\chi^{(2)})$ is assumed to be independent of the surface charge and the ionic strength. In contrast, the second term $(\chi^{(3)'} \cdot \Phi_0)$ increases with surface charge and decreases with ionic strength since the surface potential scales with surface charge and the inverse of the ionic strength (equation (2.6)). In the limit of very high ionic strengths, the v-SFG intensity is expected to be determined by the $\chi^{(2)}$ -contribution.^{25,35} In this case, a flow-induced increase in surface charge would be negligible, and no change in the v-SFG signal would be observed. With the present addition of 100 mM sodium chloride, the flow-induced increase in surface charge increases the $\chi^{(3)}$ -term. Thus, the overall v-SFG intensity still increases noticeably, but already significantly less compared to the mM concentration range for the experiment with the bare pH 3 solution (Fig. 6.3a).

While charge screening can conceptually explain the decrease in the magnitude of the normalized v-SFG intensity and the lower increase of it upon flow, one can raise the question, how big the relative contributions of the $\chi^{(2)}$ - and $\chi^{(3)}$ -term are. So far, the $\chi^{(3)}$ -term with the surface potential and its dependency on the surface charge according to equation (2.6) dominated the description of the v-SFG intensity. Accordingly, the ratio $\chi^{(3)'}/\chi^{(2)}$ as a fit parameter was rather high with 250 V⁻¹ in chapter 5 and we even neglected the $\chi^{(2)}$ -term in chapter 4. However, the results in the present chapter with the addition of 100 mM sodium chloride suggest a bigger $\chi^{(2)}$ -contribution because of the reduced flow-induced change in the v-SFG intensity and the magnitude of the v-SFG intensity itself. While the decrease in the magnitude of the v-SFG intensity with the addition of 100 mM sodium chloride is comparable with that of previous studies on the fluorite-water interface,¹⁹ much bigger drops in the intensity have been reported at the silica-water interface.^{25,99} This comparison points to a higher $\chi^{(2)}$ -contribution in the present study.

To disentangle the $\chi^{(2)}$ - and $\chi^{(3)}$ -contribution, we could assume that the addition of 100 mM sodium fluoride reduced the surface charge so much that only a $\chi^{(2)}$ -contribution is present. In

this scenario the magnitude of $\chi^{(2)}$ would only be ~10% of the v-SFG intensity obtained with the bare pH 3 (Fig. 6.1a). This, however, would be a similarly small $\chi^{(2)}$ -contribution as observed for the silica-water interface^{25,99} and would not be consistent with the small decrease of the v-SFG intensity at a 100 mM concentration of sodium chloride suggesting a higher $\chi^{(2)}$ -contribution.

To explain both, the intensity drop upon adding 100 mM sodium fluoride and the comparably small decrease in the v-SFG intensity for adding 100 mM sodium chloride at the fluorite-water interface, we can no longer assume that the $\chi^{(2)}$ -contribution is constant. It also needs to be a function of the surface charge. However, the surface charge increase upon flow is less reflected by the v-SFG intensity with the addition of the 100 mM sodium chloride, since there is only a small induced change in the v-SFG intensity compared to the bare pH 3 solution. Consequently, the description of $\chi^{(2)}$ has to be more complex. One could hypothesize that $\chi^{(2)}$ also correlates with ionic strength. Since v-SFG spectroscopy reports on the interfacial structure, a dependency on the ionic strength that influences such a structure appears reasonable. Therefore, an increase in $\chi^{(2)}$ under the investigated conditions with surface charge and ionic strength could explain the high intensity drop for the addition of adsorbing fluoride, the rather small intensity decrease upon adding 100 mM sodium chloride, and the less pronounced increase in the v-SFG intensity upon flow with 100 mM added sodium chloride.

Despite the apparent complexity of the $\chi^{(2)}$ -contribution, the lower v-SFG intensity and a less pronounced flow-induced change in that intensity with increased ionic strength can conceptually be explained by charge screening. Thus, the following investigations of other ions will be based on their sodium or chloride salt in case of an anion or cation, respectively. This allows assigning any new observation directly to the new ion. Accordingly, section 6.4 will differentiate between anion and cation interactions as the reason for decreases in the v-SFG intensity upon flow.

Similar to the addition of 100 mM sodium chloride, we observe with the addition of lithium chloride, potassium chloride, cesium chloride, and sodium bromide an increase in the v-SFG intensity upon flow that is again much lower than the one with a bare pH 3 solution (Fig. 6.4a-d and Fig. 6.1b). While lithium chloride, sodium chloride, and potassium chloride lead to almost identical changes upon flow, the one of cesium chloride and sodium bromide is a bit higher. Additionally, the magnitude of the v-SFG intensity differs for the added ions as one can see in Fig. 6.1a with almost no change for lithium chloride and a decrease of ~50% with sodium bromide, where there is also a large spread in intensities of the individual experiments. The variations between the different ions could be explained by the fact that the interfacial structure

is determined by the ionic strength and the type of ion and thus, its radius.^{25,28,62,128} Such dependencies add further complexity to the $\chi^{(2)}$ -term but also shows the limitations of the Gouy-Chapman model for screening, as it is based on the assumption of point charges. Nevertheless, the addition of lithium, potassium, cesium and bromide shows a similar behavior as sodium and chloride, which is a decrease in the magnitude of the v-SFG signal and of its flow-induced increase, which can conceptually be explained by screening. A clear correlation of the variations to properties as ionic radii is not found.



Fig. 6.4. Exemplary results of flow experiments with added LiCl, KCl, CsCl, and NaBr. Integrals of v-SFG spectra as a function of time during one flow-on/off cycle. The fluorite prism is in contact with an aqueous solution based on a pH 3 (HCl) solution to which 100 mM of the indicated salts are added. The intensities are normalized to bare pH 3 according to the average values from Fig. 6.1a. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panels shows the applied flow rate as a function of time.

6.4 Decrease upon Flow: Specific Interactions

While screening can conceptually explain a lower v-SFG intensity and the reduced increase in the v-SFG intensity upon flow, other effects must be present, when it comes to a flow-induced decrease of the v-SFG intensity. Since the interaction of sodium and chloride can be accounted for by screening, we used the sodium salts of the anions iodide and sulfate, and the chloride salts of the cations rubidium and magnesium to assign the observed decrease in the v-SFG

intensity upon flow to interactions with the anions iodide and sulfate and the cations rubidium and magnesium. In the following sections, we differentiate between the effect of the anions and the cations.

6.4.1 Anion Adsorption

The addition of the 50 mM iodide and 5 mM sulfate does not only lead to flow-induced decreases of the v-SFG intensity (Fig. 6.5 and Fig. 6.1) but also reduces the magnitude of the v-SFG intensity significantly more than the addition of 100 mM NaCl. Similar effects have been observed in chapter 5, when 1 mM sodium fluoride was added.



Fig. 6.5. Exemplary results of flow experiments with added NaI and Na₂SO₄. Integrals of v-SFG spectra as a function of time during one flow-on/off cycle. The fluorite prism is in contact with an aqueous solution based on a pH 3 (HCl) solution to which the indicated salts with the given concentrations are added. The intensities are normalized to bare pH 3 according to the average values from Fig. 6.1a. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panels shows the applied flow rate as a function of time.

To approach a possible explanation for iodide first, we propose the Gedankenexperiment that iodide behaves similar to fluoride regarding the surface charge, i.e., iodide anions can adsorb at the positively charged fluorite surface. Accordingly, the anion adsorption/desorption processes are described by equation (6.1), where X represents an adsorbing anion, i.e., fluoride or iodide.

$$\equiv CaFX(s) \rightleftharpoons \equiv CaF^{+}(s) + X^{-}(aq)$$
(6.1)

The adsorption of added iodide leads to a decrease in surface charge and thus in the magnitude of the v-SFG intensity as in Fig. 6.1a by shifting the equilibrium from equation (6.1) to the left-hand side with the lower surface charge. The dissolution of fluorite, in contrast to the surface charge, is most likely not influenced by the presence of iodide. Upon flow, the concentration of dissolved fluoride anions decreases due to dilution, which would shift the

adsorption/desorption equilibrium of only fluoride from equation (3.2) to the right-hand side with the higher surface charge. In contrast, the concentration of iodide anions remains constant as those ions are added to the bulk solution. Suppose the change in fluoride concentration is smaller than the concentration of adsorbing iodide anions. In that case, the total concentration of adsorbing anions X (fluoride plus iodide) is not significantly influenced by flow. Therefore, the new adsorption/desorption equilibrium of anions in equation (6.1) does not change. However, what is still changing upon flow is the concentration of dissolved calcium cations. In chapter 5, we showed that suppressing the flow-induced change in the concentration of adsorbing anions (there it has been only fluoride), allows for observing the flow-induced dilution of dissolved calcium cations by the decrease in the v-SFG response as a result of a shifted calcium adsorption/desorption equilibrium in equation (3.6) to the left-hand side with lower surface charges. We propose the same effect occurs upon adding iodide in the present concentration of 50 mM. To verify this hypothesis, we conducted a control experiment with aqueous solutions of sodium iodide and added calcium chloride. Based on the introduced hypothesis of iodide adsorption, one would expect that with the addition of calcium chloride the decrease in the v-SFG intensity upon flow becomes less pronounced since also the concentration of adsorbing/desorbing calcium is changing less upon flow. The experimental results are shown in Fig. 6.6a and b, confirming our hypothesis. Note, however, that calcium addition suppresses the dissolution and thus reduces the fluoride flow-off concentration in the flow channel, which, one could argue, changes the interfacial adsorption/desorption equilibria. However, the concentration of iodide is still more than two orders of magnitude higher than the ~ 0.4 mM fluoride concentration expected from dissolution.¹¹² This high concentration of an adsorbing anion suppresses a flow-induced change in the total concentration of adsorbing anions. Therefore, no shift in the adsorption/desorption equilibrium from equation (6.1) is expected. Moreover, a lower fluoride flow-off concentration due to suppressed dissolution, would lead to less pronounced changes in the anion concentration, which also suppresses a contribution from an increasing surface charge. Therefore, we are confident to connect the observed less pronounced decrease in the v-SFG intensity upon flow mainly to reduced dilution of the calcium concentration. Consequently, the observed decrease in the v-SFG intensity upon flow, observed with the iodide solution, can be explained by an additional adsorption process of the added anion. This adsorption process is also consistent with a decrease in the magnitude of the v-SFG intensity that is much higher than that due to screening, as observed for chloride at even higher concentrations.



Fig. 6.6. Verification of iodide adsorption. V-SFG intensity as a function of time during one flow-on/off cycle for different solutions the fluorite prism is in contact with. All solutions are based on hydrochloric acid (pH 3). The flow-off intensities are normalized to those of a bare pH 3 solution. The added salt and its concentration is indicated in every panel. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panel per column shows the applied flow rate as a function of time.

Since iodide readily oxidizes in the presence of water,¹²⁹ one can question whether iodide or an oxidation product is responsible for the observations. To stabilize the iodide solution, we conducted a control experiment with the addition of 2% sodium thiosulfate relative to the iodide concentration in accordance with previous studies on iodide solutions.¹³⁰ However, the addition of thiosulfate complicates the experiment, as shown in Fig. 6.6c. As little as 1 mM sodium thiosulfate leads to a slight decrease in the v-SFG intensity upon flow. Thiosulfate itself likely adsorbs at the fluorite surface. Therefore, the flow-induced change in the concentration of adsorbing anions (i.e., fluoride and thiosulfate) is suppressed to an extent where it is slightly smaller than the one of calcium, explaining a slight tendency to a flow-induced decrease. With the addition of further adsorbing anions, i.e., iodide as in Fig. 6.6d, the flow experiment exhibits again a clear decrease in the v-SFG intensity upon flow due to more suppression of the flow-induced change in adsorbing anion concentration. Considering that the addition of iodide to the thiosulfate solution also leads to a higher v-SFG intensity under flow-off conditions, it is likely that the singly charged iodide as well as the dissolved fluoride anion competes for adsorption at the fluorite surface with the doubly charged thiosulfate. Thus, adding the less negatively charged iodide anions leads to slightly higher surface charges than the solution containing thiosulfate but no iodide. This explanation further supports our interpretation of

iodide adsorption. Finally, the adsorption of iodide is consistent with its property to accumulate at aqueous interfaces due to its size and polarizability.¹³¹⁻¹³³ Those properties rationalize why the interaction between fluorite and iodide goes beyond charge screening.

According to the discussion above, not only iodide but any adsorbing anion X leads to lower v-SFG intensities and, at certain concentrations, to a decrease in intensity upon flow due to the reduced calcium concentration as a result of dilution. Consequently, those observations can be used as an indication for an adsorption process. However, an additional cause for the flow-induced decrease in the surface charge and v-SFG intensity can be the adsorption of divalent anions. According to equation (6.2), already the exchange between fluoride and sulfate can reduce the surface charge.

$$\equiv CaF^{+}(s) + SO_{4}^{2-}(aq) \rightleftharpoons \equiv CaSO_{4}(s) + F^{-}(aq)$$
(6.2)

At flow-off conditions, the magnitude of the v-SFG intensity for the adsorbing divalent sulfate ion is lower compared to the more concentrated iodide solution (Fig. 6.1a). Upon flow, dilution reduces the fluoride concentration shifting the chemical equilibrium from equation (6.2) to the right-hand side with the lower surface charge as observed in the experiment with the decrease of the v-SFG intensity upon flow (Fig. 6.5b.). Despite the exchange of a surface fluoride with a sulfate, the discussed dilution of the calcium concentration will also contribute to the decrease in surface charge. The fact that a more pronounced decrease in the v-SFG intensity upon flow is observed for the sulfate solution compared to the iodide solution might be an indication that calcium dilution alone could not be the cause for our observed decrease. Therefore, the magnitude of the flow-induced decrease as observed for the sulfate solution could support the proposed exchange reaction (6.2).

6.4.2 Cation Interactions

Apart from the presence of certain anions, rubidium and magnesium cations also lead to a flow-induced decrease in the v-SFG response (Fig. 6.7).

As for rubidium one could hypothesize that in addition to fluoride and calcium ions' adsorption/desorption processes, a rubidium-calcium exchange takes place as illustrated in equation (6.3). This reaction could also explain the reduction in the v-SFG intensity in Fig. 6.1a.

$$\equiv CaF^{+}(s) + Rb^{+}(aq) \rightleftharpoons \equiv RbF(s) + Ca^{2+}(aq)$$
(6.3)



Fig. 6.7. Exemplary results of flow experiments with added RbCl and MgCl₂. Integrals of v-SFG spectra as a function of time during one flow-on/off cycle. The fluorite prism is in contact with an aqueous solution based on a pH 3 (HCl) solution to which the indicated salts with the given concentrations are added. The intensities are normalized to bare pH 3 according to the average values from Fig. 6.1a. The added salt and its concentration is indicated in every panel. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panels shows the applied flow rate as a function of time.

According to this surface reaction, the presence of flow, i.e., dilution of dissolved calcium, shifts the chemical equilibrium to the right-hand side with lower surface charge. This process would be sensitive to the bulk calcium concentration. Therefore, one way to prove our hypothesis is by adding calcium to the bulk solution. The results of such experiments are shown in Fig. 6.8a and b. The v-SFG intensity time trace with added rubidium in Fig. 6.8a does not show a decrease this time, but no significant change at all. This observation still points to an interaction beyond screening because screening alone at the used ionic strength only reduces the observed flow-induced increase to \sim 5-10% as observed for the other alkali chlorides. Following the introduced hypothesis, it could be possible that for this measurement, the competing intensity increase upon flow due to fluoride dilution, and the intensity decrease upon flow due to calcium dilution and rubidium-calcium exchange are balanced. Interestingly, the addition of calcium to the rubidium solution leads to a decrease (Fig. 6.8b). This is not consistent with the introduced hypothesis of a rubidium-calcium exchange, because this exchange would be a contribution that decreases the v-SFG signal and should become less pronounced when calcium is added. Thus, starting from a balance between flow-induced increase and decrease as proposed for Fig. 6.8a, one would expect an intensity increase in Fig. 6.8b. Consequently, there is currently no hypothesis for the mechanism of how rubidium interacts with the charged fluorite surface. However, the interaction clearly goes beyond charge screening.



Fig. 6.8. Dependency of rubidium and magnesium interactions with the fluorite surface on calcium addition. Integrals of v-SFG spectra as a function of time during one flow-on/off cycle for different solution the fluorite prism is in contact with. All solutions are based on hydrochloric acid (pH 3). The intensities are normalized to bare pH 3. The added salt and its concentration is indicated in every panel. Each open black circle corresponds to one integrated spectrum, and the solid orange line is a ten-point moving average to guide the eye. The flow-on regions are marked with dashed grey lines. The solid black line in the bottom panel per column shows the applied flow rate as a function of time.

The observed decrease in the v-SFG intensity upon flow with added magnesium cannot be explained with an exchange reaction since magnesium and calcium are both two times positively charged. However, one could speculate about a dependency of the fluoride adsorption/desorption rate constants on the magnesium concentration. This might be consistent with the low solubility of magnesium fluoride.¹¹² In this scenario, the flow-induced effect could be dominated by calcium desorption, which means the addition of calcium would influence the flow-induced change. As one can see from Fig. 6.8c and d, the v-SFG intensity time traces of the magnesium solutions with and without added calcium are essentially identical, falsifying this hypothesis. As for now, there is also no hypothesis how magnesium could interact with the positively charged fluorite surface. At least, it is clear, that the interaction goes beyond screening. Even though the magnitude of the v-SFG signal from the magnesium solution is comparable with those of screening ions (Fig. 6.1), screening only could not explain a decrease of the surface charge and thus the v-SFG intensity upon flow.

6.5 Conclusion

We have shown that flow experiments add valuable information when it comes to the interpretation of ion-specific interactions with a charged mineral surface. In our experiments, we compared the magnitude of the v-SFG intensities at the fluorite-water interface as well as its change upon flow for the addition of different ions. Despite the demonstrated complexity underlying the v-SFG intensity, particularly the $\chi^{(2)}$ -contribution, charge screening conceptually explains a decrease in the magnitude of the v-SFG intensity and a less pronounced change upon flow. However, charge screening cannot change the sign of the flow-induced change. Such behavior can only be described by direct interaction with the surface in terms of an adsorption or exchange reaction of anions. Although some ion-specific interactions cannot yet be explained in detail, our flow experiments revealed that their interaction must go beyond screening. We expect that flow experiments will play an important role in the future for studying the interaction of ions with solid surfaces as for instances in geochemical settings like the fluorite-water interface.

7 Perspective: Dynamics and Non-equilibrium Conditions at the Fluorite-Water Interface

The previous chapters focused on the comparison of the flow-off and flow-on steady state, which give important insights on the alteration of chemical equilibria and thus the involved (adsorption/desorption) reactions. However, what has not been discussed so far is the transition from one steady state to another. In other words: What are the dynamics when switching between flow-on and flow-off conditions or when changing the flow velocity. Particularly the latter is omnipresent in natural settings, where external conditions like the weather can easily alter the flow profile. This chapter aims to provide a step towards understanding those dynamics and is part of a manuscript that is currently in preparation under the working title "Studying non-equilibrium conditions at a mineral-water interface by surface-specific spectroscopy".

7.1 Expected Dynamics upon Flow

Throughout this thesis, we have seen plots of the v-SFG intensity as a function of time for flow experiments with the sudden application of flow with a flow rate of 6 mL·min⁻¹ ($Re\approx24$), for instance in Fig. 4.1c. Such a development of the v-SFG intensity is reproduced in Fig. 7.1a. Upon flow, the v-SFG intensity rapidly rises from the flow-off steady state towards the flow-on steady state. When flow is turned off again, the intensity decreases towards the initial flow-off steady state. However, this second transition after turning off the flow takes much longer (~10 min) than the transition after starting the flow (~1 min).

As discussed in the previous chapters, the flow dilutes the solution in contact with fluorite. Since the surface charge under the present acidic conditions without added fluoride is dominated by the adsorption/desorption process of dissolved fluoride anions (see chapter 4 and 5), the flow-induced dilution decreases the fluoride concentration and shifts the adsorption/desorption equilibrium from equation (3.2) to the right-hand side with the higher surface charge. This change in surface charge is reflected by the increased v-SFG intensity. Considering the inverse relation between v-SFG intensity and fluoride concentration, we can correlate the v-SFG intensity development with a concentration development shown in Fig. 7.1b. Note that this concentration curve is only schematic. Conceptually, we can understand this concentration curve as follows. When flow is applied, the solution with the flow-off concentration is removed by the flowing liquid (advection), which happens abruptly. In contrast, when the flow is stopped, it needs some time to recreate the initial flow-off concentrations by the dissolution of the mineral and slow diffusion. Therefore, we can explain slower dynamics from the flow-on to the flow-off steady state in the concentration profile and the surface charge as well as in the corresponding v-SFG response.



Fig. 7.1. Observed v-SFG response and expected fluoride concentration during a flow-on/off cycle. (a) Development of v-SFG intensity during one flow-on/off cycle at the fluorite-water interface with a pH 3 (HCl) solution. Each open black circle represents one integrated spectrum. The solid orange line is a ten-point moving average to guide the eye. (b) Scheme of the expected development of the fluoride concentration during one flow-on/off cycle. The concentration is normalized to the flow-off saturation concentration. The degree of dilution upon flow is set comparable to the numeric simulation results (chapter 4). Advection is assigned to the sharp concentration decrease upon flow, diffusion is assigned to the slow increase after the flow stops. The bottom panels show the flow rate as a function of time.

While we can conceptually explain how the fluoride concentration changes during the flow experiment, which explains the most prominent process tracked by the v-SFG intensity, a closer look at the v-SFG intensity development reveals other interesting features. Directly after flow is applied, we observe first a small, reproducible decrease in the v-SFG intensity followed by the fast increase to the flow-on steady state. Such an initial change in the opposite direction has also been observed in other flow-experiments throughout this thesis, such as the addition of RbCl in Fig. 6.7a. As there are always different processes affecting the surface charge, for instance, fluoride and calcium adsorption/desorption as discussed in chapter 5, one could speculate that the concentration change varies for the different ions in time, for instance, due to different electrostatic interaction with the fluorite surface, e.g. the repelled calcium cations are removed faster by flow.

7.2 Observation of Initial Turbulence upon Flow

Surprisingly, the dynamics are very different from the ones discussed in the previous section, when the flow rate is changed. At high flow rates like 600 mL·min⁻¹ ($Re\approx2400$), we observe an overshoot in the v-SFG when applying flow as shown in Fig. 7.2a and b. This flow rate is two orders of magnitude higher than the ones that have usually been applied so far throughout this thesis. Here, the v-SFG intensity reaches a maximum value from which it decays to a steady state. Fig. 7.2a also shows that this behavior is reproducible. However, when comparing Fig. 7.2a and b, it becomes clear that both the decay rate and the steady state level can vary noticeably on different days. The latter has already been observed earlier in this thesis and been assigned to surface structure and reactivity variations. Nevertheless, the overall effect, in this case the overshoot is a robust observation. Another interesting observation in Fig. 7.2b is the undershoot of the v-SFG signal upon turning flow off, where a minimum of the v-SFG intensity is reached before the intensity increases again and approaches the level of the previous flow-off intensity. This undershoot is not observed every time, as shown evidently in Fig. 7.2a.

To approach an explanation of the consistently observed overshoot, we continue to approximate the v-SFG response as a measure for the surface charge and the corresponding fluoride concentration. Under this assumption, the overshoot reflects an initially higher decrease in the fluoride concentration. To explain such a concentration development over time we propose the hypothesis of an initial turbulence after which a stable laminar flow profile is formed. A chaotic movement within the aqueous phase during a turbulence would rationalize a higher dilution of the fluoride concentration close to the interface. In our setup, we minimized hindrances, but the use of the peristaltic pump,^{134,135} the curved route of the tubes, the connection between tubes and flow cell, and the route inside the cell could cause turbulences. Additionally, the lifetime of the turbulence might be sensitive to small experimental deviations as the surface roughness or how tubes and fluorite prism are connected to the flow cell. Such sensitivity could explain why we observe day-to-day variations in Fig. 7.2a and b.



Fig. 7.2. Observation of an overshoot in v-SFG intensity upon flow attributed to turbulences. Development of v-SFG intensity during flow-on/off cycles at the fluorite-water interface with a pH 3 (HCl) solution at a high flow rate of 600 mL·min⁻¹ ($Re\approx2400$). The intensities are normalized to the first spectrum. The solid orange line is a ten-point moving average to guide the eye. (a) Two identical cycles at a high flow rate. (b) Same as (a) but measured on another day and with only one flow cycle. (c) Same as (b) but with the addition of 4 mM sodium fluoride to the bulk solution.

To prove that the observed overshoot is directly connected to the fluoride concentration, we performed a control experiment, where we added 4 mM sodium fluoride to the aqueous phase. At such fluoride bulk concentrations, we have previously not observed any change upon flow at the lower flow rates (Fig. 4.7 and Fig. 5.1c). We expect that with such a high fluoride bulk concentration, even with turbulence, the fluoride concentration at the interface would not increase upon flow. This expectation is confirmed by the constant v-SFG intensity shown in Fig. 7.2c during a flow experiment with a high flow rate of 600 mL·min⁻¹ and 4 mM fluoride bulk concentration. Consequently, the overshoot is due to an initially lower fluoride concentration at the interface. The only explanation that we see for this is radial mixing as it occurs during turbulence. Nevertheless, it appears highly interesting to simulate the transition from turbulent to laminar flow and the corresponding concentration profile to further confirm our explanation.

Transitions from laminar to turbulent flow and vice versa have been the subject of previous studies, focusing mainly on changes in the Reynolds number and following the flow profile downstream.¹³⁶⁻¹⁴¹ Our approach differs from such studies as we investigate one position within a flow channel over time. The proposed initial turbulences is an issue which to the best of our knowledge, has not yet been discussed in literature. In contrast, an initial effect known in literature is the start-up response of the laminar velocity profile.^{142,143} However, this process occurs usually on a seconds time scale and does not include a turbulent behavior.¹⁴² When it comes to developed turbulent flow, it has been shown that a conversion to laminar flow can occur over long time scales (i.e., years).137 When comparing the time needed to reach the flow-on steady state of the v-SFG intensities in Fig. 7.2, one should realize that our experiments do not directly probe the flow profile but rather the fluoride concentration closest to the interface as this is connected to the surface charge by adsorption/desorption processes. Therefore, even if the laminar profile is already reached after an initial turbulence, we expect that it takes some time to create the flow-on steady state concentration via dissolution of the mineral and diffusion. In conclusion, however, our proposed initial turbulence is most likely neither on a time scale of seconds as the start-up response of laminar flow, nor on very long time scales as the decay of a developed turbulent flow.

In order to characterize the overshoot further, we conducted flow-on/off cycles with changing the flow rates. The measured v-SFG intensity during those cycles is shown in Fig. 7.3a. The overshoot is observed over a wide range of flow rates. However, the overshoot's maximum value decreases with the flow rate until it vanishes completely without a sharp transition. This decrease of the overshoot with decreasing flow rates might be consistent with more intense radial mixing or longer initial turbulences at higher flow rates leading to lower interfacial fluoride concentrations.

Interestingly, also the transition from the flow-on steady state to the flow-off steady state exhibits a flow rate dependency. The higher the flow rate, the faster this transition, for instance 1-2 minutes at the highest flow rates and over 10 minutes at the lowest. We quantify this flow rate dependency by a decay rate as shown in Fig. 7.3b. The decay rate is obtained by fitting the intensity development between two flow-on regimes with an exponentially decaying function as shown by the solid red lines in Fig. 7.3a. Since those fits do not capture the precise developments at later times between 6 and 60 mL·min⁻¹, one should treat the decay rates rather carefully. Nevertheless, the trend of increasing decay rates with increasing flow rates becomes clear. Correlating this decay of the v-SFG intensity with restoring the interfacial fluoride concentration from the previous flow-off state, we want to consider the gradient in the concentration profile into the solution upon flow as in chapter 4 (Fig. 4.5c). The higher the flow

rate, the steeper this gradient is. The gradient correlates with the dissolution rate according to equation (3.14). Upon switching off the flow, the concentration in the region closest to the interface increases faster, if the flow rate was higher due to the increased dissolution rate. Note that this is only valid for the interfacial concentration, which determines the surface charge and thus the v-SFG intensity. We cannot comment on the full concentration profile.



Fig. 7.3. Flow rate and position dependency of the turbulence. (a) V-SFG intensity development during flow-on/off cycles at the fluorite-water interface with a pH 3 (HCl) solution at different flow rates between 3 and 600 mL·min⁻¹ (12 < Re < 2400). The intensities are normalized to the first spectrum. The solid orange line is a ten-point moving average to guide the eye. The solid red lines are exponential fits of the flow-off decays. The applied flow rates are indicated in the lower panel. (b) Decay rates of the transition from flow-on to flow-off intensities. The rates arise from fitting the decay with an exponential function as shown in part (a). (c) As (a) but only two flow cycles with different flow directions. The experiment was conducted at 8 mm distance from the center (total channel length: 24.8 mm) with a flow rate of 60 mL·min⁻¹ ($Re \approx 240$).

Next, we want to comment on the steady state level of the flow-on intensities. As it is clear from Fig. 7.3a, the steady state level is hardly changing between 30 and 600 mL·min⁻¹. Those flow rates correspond to Reynolds numbers of ~120 and ~2400. Only at the lowest flow rates investigated here, we start to observe a dependency of that level of the v-SFG intensity upon flow. This is consistent with the discussion of a high flow-rate limit in section 4.5. There we discussed that at high flow rates, the fluoride concentrations are expected to reach a constant

value independent of the flow rate. Still the level in the v-SFG intensity of the overshoot is higher than the high-flow rate level. This can be rationalized with the idea of a layer as shown in Fig. 4.5b, that still persists at high flow rates. This layer is only perturbed upon a turbulence, which leads to such low fluoride concentrations causing the overshoot. As discussed in section 4.5, the concentration at the interface does not only get independent from the flow rate but is also equal across the mineral's surface. With Fig. 7.3c, we provide evidence for such a breakdown of the concentration gradient. As shown in Fig. 7.3c, where we measured 8 mm distance from the center, the steady states in the two flow-on regimes are roughly at the same level. Since the position chosen for measuring is not in the flow cell's center (but at roughly 1/3 of the channel length from the inlet), different positions relative to the flow coordinate are probed when the flow direction is inversed as discussed in section 4.2. Different to Fig. 4.2, the steady state levels are rather similar at the ten times higher flow rates used in Fig. 7.3c. Therefore, the data shown in Fig. 7.3c are consistent with a break-down of the concentration and surface charge gradient at high flow rates.

In contrast to the steady state flow-on v-SFG intensities along the mineral, the overshoots in the v-SFG intensity reach different levels in Fig. 7.3c. The lower level of the overshoot of the second flow cycle in Fig. 7.3c, i.e., measuring closer to the outlet, could indicate the decay of the turbulence, i.e., less radial mixing. However, the 1.6 cm difference inside the flow cell might be too small to sufficiently decay the turbulence.¹³⁷ An additional explanation could be an uptake in concentration along the channel. Even though the bulk concentration can not be expected to change significantly, the volume perturbing the interfacial concentration, may increase in fluoride concentration along the flow channel. Accordingly, the overshoot reaches a lower level as observed. Both explanations, a decay of the turbulence along the channel or a gain in concentration, are possible, alone or together, as we can not exclude either of them. Finally, we note that in this experiment, we observe again an undershoot after flow is turned off but only when measuring in clock-wise flow direction, i.e., closer to the inlet upon flow. Since this effect is not observed every time, it is hard to interpret it also in the light of a position dependency relative to the flow direction.

7.3 Experiments with Steadily Changed Flow Rates

After discussing the sudden application of flow, we want to look into a change of the flow velocity by steadily changing it. The development of the v-SFG intensity over four cycles is shown in Fig. 7.4, where the flow rate is varied between zero (i.e. flow-off) and a maximum value, with changing frequencies and maximum flow rates. The bottom panels show the cyclic variation of the flow rate and give the frequencies. The top and middle panels show the v-SFG intensity developments for the maximum flow rates of 600 and 12 mL·min⁻¹, respectively. Those flow rates correspond to Reynolds numbers of ~2400 and ~50.

In the top panel of Fig. 7.4a, the v-SFG intensity is shown for a cyclic variation of the flow rate with a frequency of 0.5 mHz and a maximum flow rate of 600 mL·min⁻¹. The v-SFG intensity development shows non-identical and asymmetric cycles. The maximum of the v-SFG intensity is observed at a flow rate lower than the maximum. This mismatch of the v-SFG intensity and flow rate maxima is indicated by the dashed grey lines in Fig. 7.4, which mark the maximum flow rates. We consider this early maximum in the v-SFG intensity similar to the previous section as an overshoot. As for the previous section, such an overshoot could be consistent with turbulence that arises at a certain flow rate below the maximal one. This means that after the overshoot, the flow profile becomes again rather laminar. Accordingly, the fluoride concentration has a minimum during the turbulence and increases again afterwards even though the flow rate is still rising. Interestingly, this overshoot is most pronounced in the first cycle. From the second cycle onwards, there seems to be a smaller but steady intensity decrease. For the first cycle it might be possible that the development of the flow and concentration profile is different because the system was in a flow-off steady state before. Another observation is the steeper increase in the v-SFG intensity at lower flow rates. This is consistent with a transition from the low to the high flow-rate limit. Only in this transition regime, a flow-rate dependency on the dilution is expected.

The middle panel in Fig. 7.4a shows the v-SFG intensity development during the cyclic change of flow rates with a frequency of 0.5 mHz as in the top panel but with only 12 mL·min⁻¹ as maximum flow rate. As discussed earlier, with this maximum flow rate, the high flow rate limit is not reached and turbulences are not expected. Accordingly, an almost linear change of the v-SFG intensity with the flow rate change is observed. Additionally, the v-SFG intensity cycles are rather symmetric and very similar, with no mismatch between the flow rate and the v-SFG intensity maxima as indicated by the dashed grey lines.



Fig. 7.4. V-SFG response to the cyclic variation of the flow rate. Development of the v-SFG intensity over time at the fluorite-water interface with a pH 3 (HCl) solution for a continuous variation of the flow rate. Each open black circle in the top and middle panels correspond to one integrated spectrum. The intensities are normalized to the first spectrum. The solid orange line is a ten-point moving average to guide the eye in (a) and a three-point moving average in (b). The bottom panel shows the cyclic variation of the flow rate normalized to the maximum value. Top and middle panels indicate the maximum flows rate used. **(a)** Slow variation of flow rate with a frequency of 0.5 mHz. **(b)** Fast variation of flow rate with a frequency of 10 mHz. The dashed grey and blue lines indicate the time of the maximal flow rate and zero flow rate (i.e. flow off), respectively.

Comparing the top panels of Fig. 7.4a and b with 600 mL·min⁻¹ as maximum flow rate but different frequencies for the flow rate changes, it becomes clear that some information on the dynamics is lost at the higher frequency. For instance, there are no overshoots in the individual cycles and the cycles are much more similar, with only the first one in the top panels of Fig. 7.4b reaching slightly higher intensities. Accordingly, the cycles in the top panels of Fig. 7.4b are also more symmetric with no clear mismatch of the flow rate maxima and the v-SFG intensity maxima as indicated by the dashed grey lines. When comparing next the level of the flow-induced increase of the cycles for both frequencies in the two top panels, one notices that with the higher frequency in Fig. 7.4b, the increase is always higher as for the slow changes in Fig. 7.4a. Additionally, it seems that a plateau is reached at high flow rates with the fast change in the flow rates, although it is, of course, hard to tell from the few data points in the top panel of Fig. 7.4b. Connecting these observations to the explanation of the flow and concentration profile, it appears likely that with the fast flow rate changes in the top panel of Fig. 7.4b during the high flow rates over the \sim 6 spectra at similar intensity turbulences are present. With the faster change of the flow rates in Fig. 7.4b, i.e., bigger steps between two flow rates, persisting turbulences might appear plausible.

Comparing the middle panels of Fig. 7.4 with the lower maximum flow rate, one notices that the v-SFG intensity maxima reach similar values at both frequencies of the flow rate changes. This is in contrast to the higher flow rates from the top panels. This contrast is consistent with the explanation of turbulences, which are not expected at the lower flow rates. Therefore, more similar levels of the v-SFG intensity maxima are reached in the middle panels.

Due to the steady change of the flow rate, the system is after the initial flow-off steady state never equilibrated. Already the experiments with an abrupt application of flow showed that even without an overshoot, it takes several spectra before a steady state is reached. This missing equilibration in the current experiments becomes even more evident from v-SFG intensity minima. In Fig. 7.4b, the v-SFG intensity minima after the initial flow-off steady state do not reach the level of the initial steady state. This can be explained by the long time it takes to restore the flow-off fluoride concentration, as discussed in the context of Fig. 7.1. Another interesting observation is the phase mismatch of the minima in v-SFG intensity and the flow rates as indicated by the dashed blue lines in Fig. 7.4 that go through the flow rate minima (i.e., flow-off). Each v-SFG intensity minimum in Fig. 7.4 is shifted to later times than the flow-off time (i.e., minimum in flow rate). This mismatch is particularly prominent at lower maximum flow rates in the middle panel in Fig. 7.4. Such a mismatch can be explained by the limit of low flow rates that has already been mentioned in section 4.5. After the flow rate minimum (flow-off), the advection of the first applied flow rates is too weak to decrease the concentration close to the interface noticeably. In fact, the fluoride concentration is still rising as it becomes clear from the still decreasing v-SFG intensity. This rise in concentration means that the concentration increase by dissolution and diffusion from the surface is higher than the removal by advection. With increasing flow rates, a minimum of the v-SFG intensity is passed, which means that the fluoride concentration starts to decrease. At this point, the system leaves the low flow rate limit, i.e., advection overcomes diffusion.

Finally, we want to point again to a small decrease in the v-SFG intensity when liquid flow is applied after an initial flow-off steady state. We observe this behavior in all shown intensity developments, although for the top panel of Fig. 7.4b, it is only one data point.

7.4 Conclusion

In conclusion, this chapter illustrates the complexity of non-equilibrium conditions at the fluorite-water interface by studying the v-SFG intensity to measure the surface charge and the corresponding interfacial fluoride concentrations. The observation of an initial overshoot in the v-SFG intensity upon applying high flow rates can be explained by the presence of turbulences, which can vanish over time, allowing the flow and concentration profiles to equilibrate. Further verifications of this hypothesis would probably require complex simulations of those profiles' temporal development. Such a simulation could also be used to investigate the influence of the concentration gradient into the solution upon flow on the dynamics when stopping the flow. Furthermore, the application of continuous flow velocity changes is connected to the high and low flow rate regimes from chapter 4. Finally, there are still some dynamics that are not yet completely understood, like the very initial decrease of the v-SFG intensity upon flow or a possible undershoot after stopping the flow.

8 Outlook

The present thesis showed which insights surface-specific v-SFG spectroscopy can provide on the fluorite-water interface upon flow. The enhanced understanding of the interfacial events upon flow, which are presented in chapter 4, are the foundation to develop a highly sensitive approach to disentangle surface reactions as demonstrated in chapter 5. Therefore, this thesis paves an experimental way to uncover the interfacial chemistry, particularly at mineral-water interfaces, as required for geochemical modeling. It is proven, in chapter 6, also for the fluorite-water interface that this approach can be applied to study ion-specific interactions. While not all interactions between the investigated ions and the fluorite surface have been completely understood yet, it is clear that the characteristics of a flow experiment add important information that can be essential for our understanding. Consequently, it can be expected, that future (spectroscopic) studies of mineral-water interfaces include flow experiments as in this thesis. Furthermore, the concept of spectroscopically following a flow-induced concentration change can also be used to study surface reactions within more applied systems, as in electrochemistry or heterogeneous catalysis.

In addition to applying the developed approach to other relevant systems, some questions are raised within this thesis that might be worth addressing in the future. In chapter 5, we observed that flow-induced changes at a certain fluoride concentration can behave differently depending on the sample's history, i.e., not measuring a series of concentrations consecutively. This history-dependency might be an indication of a memory effect of the surface. To look further into this behavior, imaging methods like AFM might add valuable information. Particularly, operando AFM studies on our solid-liquid interface upon flow could be useful to understand how the fluorite surface changes over time. In chapter 6, the complexity of the v-SFG intensity regarding the ratio of $\chi^{(2)}$ and $\chi^{(3)}$ as well as its dependency on surface charge and ionic strength have been demonstrated. However, an accurate model or description is missing so far. In order to develop a detailed understanding, one would need to investigate the v-SFG intensity systematically as a function of surface charge and ionic strength over a wide range. To scan this parameter space, the surface charge could be controlled by the addition of sodium fluoride and the ionic strength by the addition of sodium chloride. Further questions raised in chapter 6 pertain to the fluorite surface's interactions with some ions, particularly how these ions lead to the flow-induced change in the v-SFG intensity. Some of these results have not even conceptually been understood. This clearly requires the development of additional models of interaction. Again imaging methods like AFM, might contribute in this regard, if intercalation of the added ions occurs. Additionally, the ion's interaction could be addressed by computational methods providing a molecular picture of the events at the interface. Finally, in chapter 7, the non-equilibrium conditions of the fluorite-water surface are investigated, which leads to the observation of effects that are worth to be studied further. Particularly the raised hypothesis of initial turbulences could be addressed by simulations of the flow system. However, such a simulation would have to reflect the precise setup rather accurately and would benefit from a high resolution due to the small probing depth of the spectroscopic method. Such an approach can be expected to be currently computationally rather expensive. Nevertheless, such simulations might also provide insights on very initial processes when applying flow or stopping the flow.

Apart from flow-induced changes in concentrations that affect the surface chemistry and thus a v-SFG response, it might be interesting to study the evolution of the EDL or even of the first layer of interfacial water molecules upon flow further. To do so, one needs a system where the flow-induced change is not dominated by this change in concentration. One could think about an inert material as diamond for the solid phase. To see whether the friction upon flow does alter the orientation of water molecules is interesting because, in the macroscopic description of water, it is considered a continuous medium, which is certainly not the case. Such an investigation may profit from molecular simulations as well as phase-resolved v-SFG measurements. Such measurements might also be interesting not only in the OH stretch region as in the present study but also in the region of the water bending mode (~1600 cm⁻¹). To study the influence of a surface charge in connection to friction or to study the EDL at a solid-liquid interface upon flow, a constant surface charge would be desirable. This can be achieved by using, for instance, graphene attached to glass. If it is less about the structure of the water molecules but the surface charge and ion distribution, SHG experiments could also be considered.

In conclusion, the scientific findings of this thesis provide tools for an educated investigation of other systems, for instance, the geochemically relevant silica-water or sapphire-water interface but also more technologically relevant interfaces occurring in electrochemistry or heterogeneous catalysis. The underlying concepts found for the fluorite-water interface can be easily transferred. Furthermore, by targeting the fluorite-water interface under different conditions, from which most has already been conceptually understood, some remain unclear and can thus be the objective for future studies. Finally, there are more details one can look into concerning the description of the v-SFG intensity itself or the degree to which friction upon flow alters interfacial structures.

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List of Abbreviations and Symbols

Latin Symbols

Symbol	Meaning	Unit
а	acceleration	$m \cdot s^{-2}$
Α	adsorbing particle	
a _s	exchange area	m ²
A_{γ}	IR transition dipole moment	A · s · m
С	concentration	$mol \cdot m^{-3}$
d	differential	
$d_{ m p}$	diameter of pipe	m
D	diffusion coefficient	$m^2 \cdot s^{-1}$
div	divergence	
E	electric field	$V \cdot m^{-1}$
f _{corr}	correction function for pH change	
f_3	coherence term	
grad	gradient	
Н	height	m
I _c	ionic strength	$mol \cdot m^{-3}$
Ι	intensity	$J \cdot s^{-1} \cdot m^{-2}$
i	imaginary unit	
J	flux	$mol \cdot m^{-2} \cdot s^{-1}$
k _{ads}	rate constant adsorption	s ⁻¹
k _{des}	rate constant desorption	$mol \cdot m^{-3} \cdot s^{-1}$
k _{dis}	rate constant dissolution	$mol \cdot m^{-2} \cdot s^{-1}$
k _{prec}	rate constant precipitation	$m^7 \cdot mol^{-2} \cdot s^{-1}$
L	length	m
L _C	length of flow channel	m
L _{CaF2}	solubility product of fluorite	
L _S	length of reactive surface	m
L _R	length of reservoir	m
L _{ii}	Fresnel coefficient	
L _{slip}	slip length	m
$M_{\alpha\beta}$	Raman transition dipole moment	$A \cdot s \cdot m^2 \cdot V^{-1}$
n _i	refractive index of medium i	
n	surface normal	
Ν	number of molecules per volume	m ⁻³
<i>p</i>	pressure	$kg \cdot m^{-1} \cdot s^{-2}$
Р	polarization	$A \cdot s \cdot m^{-2}$

Pe	Péclet number	
r	radial coordinate	m
R	radius	m
r _c	chemical reaction rate	$mol \cdot m^{-3} \cdot s^{-1}$
$R(\psi_{\rm E})$	rotation matrix using Euler angle $\psi_{ m E}$	
$R(\phi_{\rm E})$	rotation matrix using Euler angle $\phi_{ m E}$	
$R(\theta_{\rm E})$	rotation matrix using Euler angle $ heta_{ m E}$	
Re	Reynolds number	
S	surface (site)	
SA	occupied surface site	
Sh	Sherwood number	
t	time	S
Т	temperature	К
u	velocity	$m \cdot s^{-1}$
x	position	m
x _{CaF₂}	amount of dissolved CaF ₂	$mol \cdot m^{-3}$
X	adsorbing anion	
Ζ	valence	

Greek Symbols

Symbol	Meaning	Unit
α	polarizability	$A \cdot s \cdot m^2 \cdot V^{-1}$
β_i	mass transfer coefficient of component i	$m^2 \cdot s^{-1}$
β	first-order hyperpolarizability	$A \cdot s \cdot m^3 \cdot V^{-2}$
γ	second-order hyperpolarizability	$A \cdot s \cdot m^4 \cdot V^{-3}$
γ _r	refracted angle	0
Γ	density of surface sites	m ⁻²
δ	effective dilution	
Δ	difference	
<i>e</i> _r	relative permittivity	
η	dynamic viscosity	$kg \cdot m^{-1} \cdot s^{-1}$
θ	angle of incidence	0
$\theta_{\rm C}$	angular coordinate in flow channel	0
$ heta_{ m E}$	Euler angle	0
к	electrical conductivity	$A \cdot V^{-1} \cdot m^{-1}$
$\lambda_{\rm D}$	Debye screening length	m
μ	dipole moment	$A \cdot s \cdot m$
ν	frequency	s ⁻¹
ν _i	stoichiometric number of component i	
$\chi^{(1)}$	susceptibility	

$\chi^{(2)}$	second order susceptibility	$m \cdot V^{-1}$
$\chi^{(3)}$	third order susceptibility	$m^2 \cdot V^{-2}$
$\chi^{(3)'}$	effective third order susceptibility	$m \cdot V^{-2}$
ρ	density	$kg \cdot m^{-3}$
σ	surface charge density	$A \cdot s \cdot m^{-2}$
$\sigma_{\rm V}$	charge density	$A \cdot s \cdot m^{-3}$
Σ_i	sum over i	
τ	relaxation time	S
$\phi_{ m E}$	Euler angle	0
Φ	potential	V
Φ_0	surface potential	V
Φ_{ζ}	zeta potential	V
$\Phi_{ m stream}$	streaming potential	V
$\psi_{ m E}$	Euler angle	0
ω	angular frequency	s ⁻¹
ων	frequency of a resonance	S ⁻¹

Constants

Symbol	Meaning	Value and Unit
е	elementary charge	$1.60 \cdot 10^{-19} \mathrm{A} \cdot \mathrm{s}$
exp	Euler constant	2.72
g	gravitational acceleration	$9.81 \text{ m} \cdot \text{s}^{-2}$
h	Planck constant	$6.63 \cdot 10^{-34} \text{ J} \cdot \text{s}$
k _B	Boltzmann constant	$1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$
N _A	Avogadro constant	$6.02 \cdot 10^{23} \text{ mol}^{-1}$
ϵ_0	electric permittivity of vacuum	$8.85 \cdot 10^{-12} \text{ A} \cdot \text{s} \cdot \text{ V}^{-1} \cdot \text{m}^{-1}$
π	Archimedes constant	3.14

Lower Indices

Index	Meaning
А	adsorbing particle
b	bulk
DC	direct current
eff	effective
i	index of solution or ion or a room coordinate
IR	infrared

j	index for a room coordinate
k	index for a room coordinate
max	maximum value
Off	Flow off condition
On	Flow on condition
р	p-polarized
S	s-polarized
S	surface (site)
SA	occupied surface site
SFG	Sum Frequency Generation
tot	total
Vis	visible
X	room coordinate
У	room coordinate
Z	room coordinate
1	counter of radiation or medium
2	counter of radiation or medium
α	molecular coordinate
β	molecular coordinate
γ	molecular coordinate
0	before HF formation

Abbreviations

Abbreviation	Meaning
AOM	acousto-optic modulator
EDL	Electrical Double Layer
DFG	Difference Frequency Generation
GVD	group velocity dispersion
h	horizontal
IHP	Inner Helmholtz Plane
IR	infrared
NDFG	Non-collinear Difference Frequency Generation
OHP	Outer Helmholtz Plane
SFG	Sum Frequency Generation
SHG	Second Harmonic Generation
v	vertical
Vis	visible
v-SFG	vibrational Sum Frequency Generation

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