Article

Ion-Specific Interactions at a Mineral-Water Interface Revealed by Surface-Sensitive Spectroscopy under Flow Conditions

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ABSTRACT: A solid surface in contact with an aqueous solution is typically charged. When put in contact with an aqueous electrolyte solution, the surface charge and composition are crucially affected by the composition of the aqueous phase due to ion-specific interactions between ions and the solid surface. In this study, we combine surface-sensitive vibrational sum frequency generation (v-SFG) spectroscopy and flow experiments to investigate ion-specific interactions at the fluorite-water interface. The flow-induced change in the concentration of dissolved ions at the surface shifts chemical equilibria and can therefore influence the surface potential, which we probe by the v-SFG intensity in the OH stretch region. By studying the v-SFG intensity and its flow-induced change for different salts, we identify charge screening and ion-specific effects, including surface adsorption.
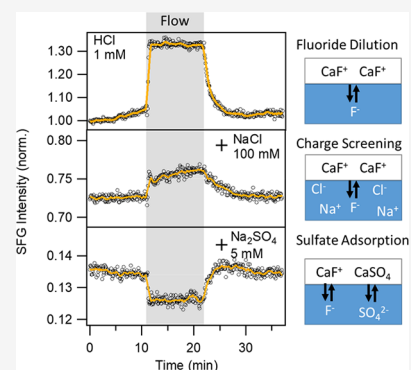
INTRODUCTION

Whether it is on the ground of the ocean or simply a stone in a river, mineral-water interfaces are ubiquitous in natural settings, with the mineral typically being charged due to the release of ions upon dissolution. A molecular picture of the interfacial chemistry at such interfaces is crucial for understanding and modeling geochemical processes like remediation.[1,2] The interfacial chemistry at the mineral-water interface can be affected by the presence of different ions, which is why there are numerous studies elaborating on ion-specific interactions at charged mineral-water interfaces.[3−10] Such interactions include the screening of the surface charge by direct adsorption on the surface, or by near-surface accumulation in the Stern layer. In both cases, the interfacial water bonding structures will be affected.[8]

To investigate how ions specifically interact with a charged mineral surface, nonlinear optical spectroscopy provides a powerful tool as it is sensitive to symmetry-broken environments that usually occur at surfaces. For instance, the intensity in a vibrational Sum Frequency Generation (v-SFG) spectrum I_{SFG} in the O−H stretch region scales with the surface potential since it probes the net orientation and polarization of near-surface water molecules. This correlation is commonly expressed by eq 1, where Φ_0 is the surface potential and $\chi^{(2)}$ and $\chi^{(3)}$ denote the second- and third-order nonlinear susceptibility, respectively.

$$I_{SFG} \sim |\chi^{(2)} + \chi^{(3)} \cdot \Phi_0|^2 \tag{1}$$

According to the Gouy−Chapman model, the surface potential depends on the surface charge σ as well as the ionic strength I of the aqueous solution, screening the polarization into the solution. Mathematically, those dependencies can be expressed via eq 2, where k_B is the Boltzman constant, T is the temperature, e is the elementary charge, N_A is Avogadro's constant, ε_0 is the vacuum permittivity, and ε_r is the relative permittivity of the medium (aqueous solution), i is index for the ion, z_i is the charge of that ion, and $c_{i,\,bulk}$ is the concentration of that ion in the bulk.[11−14]

$$\Phi_0 = \frac{2k_B T}{e} \cdot \sinh^{-1}\left(\frac{\sigma}{\sqrt{8k_B T N_A I \varepsilon_0 \varepsilon_r}}\right) \text{ with } I = \frac{1}{2}\sum_i z_i^2 c_{i,bulk} \tag{2}$$

The $\chi^{(3)}$-term of eq 1 can be expanded by an interference term, which accounts for the interference between SFG radiation generated from different layers within the electric double layer (EDL) that can significantly influence the observed SFG intensity. The lower the ionic strength, the thicker the EDL, which is why interference is becoming relevant for ionic strengths below 1 mM. Additionally, the
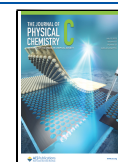
penetration depth of the local fields depends on the incident angles. For total internal reflection (TIR) experiments, the effect of interference from the EDL is additionally limited by the rapid decay of the evanescent field into the solution.[11,12,15,16] In the present study, we apply total internal reflection to study the interface of an aqueous solution based on 1 mM HCl solution with the addition of more than 1 mM salts. Therefore, the interference term can be neglected; we are always above the critical concentration of 1 mM. Equations 1 and 2 show that the v-SFG intensity depends on the surface charge and the interfacial ion concentration. Therefore, it remains challenging to differentiate between different effects. For instance, an increase in ionic strength can lower the surface potential and, thus, the magnitude of the v-SFG intensity. However, the same is true for a counter ion adsorbing from the solution to the oppositely charged surface, which lowers the surface charge and thus surface potential and the observed v-SFG intensity. In order to truly identify the ion-specific interactions, we need additional insights. One approach can be combining v-SFG spectroscopy and flow experiments. As we have concluded recently,[17,18] the application of flow dilutes the concentration of dissolved ions and therefore shifts adsorption/desorption equilibria of those ions, which then changes the surface charge. From differences between flow-off and flow-on spectra, we disentangled Ca^{2+} and F^- ion adsorption at the interface between the common mineral fluorite (calcium fluoride, CaF_2) and water. In this study, we use this approach to learn more about ion-specific interactions at the fluorite-water interface as a model system.

■ EXPERIMENTAL SECTION

V-SFG Spectroscopy. The v-SFG data presented in this work are recorded with an experimental setup that has been described previously.[18] All spectra are recorded in ssp polarization combination (s-polarized SFG, s-polarized visible, and p-polarized IR) and at incident angles $\theta_{vis} \approx 74°$ and $\theta_{IR} \approx 80°$ of the visible and infrared pulse, respectively. Those angles varied between the conducted experiments over some degree due to changes in the alignment. However, within one series of measurements at one day, the alignment was not touched after initial optimization. Such large angles were chosen to enable total internal reflection experiments, which allow for high signal-to-noise ratios and thus acquisition times of 5 s per spectrum. We were therefore able to follow the v-SFG intensity as a function of time over during the flow experiment, as can be seen in Figure 1a.

Sample Preparation. The rectangular fluorite prism (dimensions 4 cm × 1 cm × 0.5 cm) purchased from EKSMA optics was baked at 500 °C for at least 2 h to remove organic residues. Before and after baking, it was rinsed with demineralized water and filtered with a Millipore unit (resistivity = 18 MΩ cm). The salt was added to a 1 mM solution of hydrochloric acid, which was prepared by volumetric diluting concentrated acid (37 w%) with Milli-Q water. Details about the chemicals can be found in the SI.

Flow Setup and Experimental Procedure. The flow setup and the experimental procedure are described in our previous work (ref 18). Spectra were recorded at the center of the flow channel. The flow rate was ∼6 mL/min, corresponding to a Reynolds number of ∼25 and a shear rate of ∼9 s^{-1} ensuring laminar flow. 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
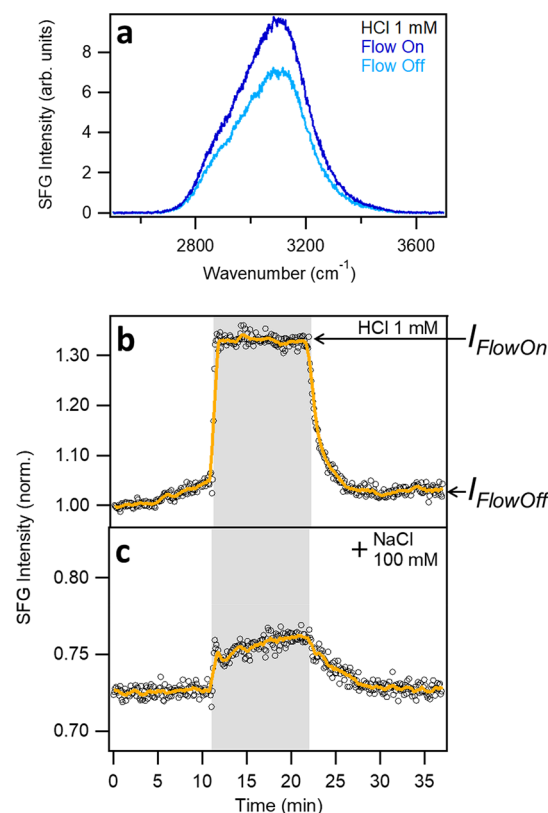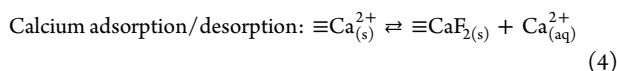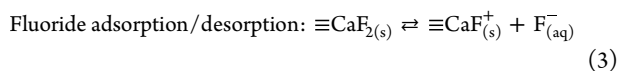

Figure 1. Fluid flow reversibly changes the surface potential. (a) V-SFG spectra in the OH stretch region from the fluorite-water interface with 1 mM HCl in the aqueous solution under flow-on and flow-off conditions. The flow rate upon flow was 6 mL·min^{-1}, corresponding to a Reynolds number of ∼25. Note that the spectra are not normalized to the shape of the IR pulse since this is challenging when the experiment is performed under total internal reflection geometry.[19] (b) V-SFG intensity as a function of time during one flow-on/off cycle. Every open black circle represents one integrated spectrum as in (a). The spectra were integrated between 2500 and 4000 cm^{-1} and normalized to the first integral. The flow-on region is highlighted in gray. The solid orange line is a ten-point moving average to guide the eye. The arrows mark the intensity level of the flow-on and flow-off state. (c) Same as (b) but with the addition of 100 mM NaCl to the aqueous phase and the intensity of the first spectrum being normalized to that of the bare 1 mM HCl solution from (b).

diameter: 8.0 mm). A homemade LabView program controls the peristaltic pump (Masterflex 77924-70 L/S Ethernet/IP Network-Compatible Pump). For the flow experiments, we waited at least 5 min before recording the first flow-off spectrum of the series of spectra and took 5 s spectra.

Data Processing. The spectra were processed by a self-written MatLab script, which has been described in ref 18, resulting in time traces of the v-SFG intensity as shown in Figure 21b. In some experiments, the v-SFG intensity shows an unspecific drift, on top of which the flow-induced changes occur. To extract the flow-induced changes, the data were corrected as described in ref 17. The relative changes were calculated based on averaging the corrected intensities of the last minute before switching between flow on/off, where an equilibration of the concentration and surface charges can be assumed.

RESULTS AND DISCUSSION

We conducted flow experiments with flow-on/off cycles at the fluorite-water interface under slightly acidic conditions (1 mM HCl) with and without the addition of various salts. We detected the v-SFG intensity as a function of time to measure the surface potential. Figure 1a shows two spectra in the OH stretching region for a 1 mM HCl solution (no salts added) in contact with fluorite. It should be noted that for the discussion of the investigated changes in the surface potential, it is sufficient to consider the v-SFG intensity as derived from the integration of the unnormalized spectra, as we justify in Section S2 of the SI, where we also show a normalized spectrum. We also comment in S3 of the SI on the small effect of the switch between ions on the spectral shape. As shown and discussed in previous studies,[17−20] the spectrum obtained under flow-on conditions is substantially increased in its spectral intensity. As shown in Figure 1b, we quantify this increase by showing the v-SFG intensity (integral over the OH stretch region between 2500 and 4000 cm^{-1}) as a function of time over one flow-on/off cycle. From this plot, one can see that the flow-induced increase is ∼30% and reversible, i.e., upon stopping flow, the intensity returns to its initial level. This observation has been explained in our previous work by an increased surface charge upon flow[19] since flow reduces the interfacial concentrations of the dissolved fluoride and calcium ions due to dilution.[17,18] This concentration changes shift the adsorption/desorption equilibria (eqs 3 and 4) to the right-hand side, where ≡ denotes the solid CaF_2 subphase.

Fluoride adsorption/desorption: $\equiv CaF_{2(s)} \rightleftarrows \equiv CaF_{(s)}^{+} + F_{(aq)}^{-}$ (3)

Calcium adsorption/desorption: $\equiv Ca_{(s)}^{2+} \rightleftarrows \equiv CaF_{2(s)} + Ca_{(aq)}^{2+}$ (4)

Due to the dominance of the fluoride adsorption/desorption reaction under the investigated conditions, those observations can be mainly assigned to enhanced fluoride dissolution upon the reduced fluoride concentration during the flow-on period.[17] Consequently, the surface charge is increased upon flow, which gives rise to higher v-SFG intensities.

Interestingly, upon the addition of 100 mM NaCl (see Figure 1c), two effects are observed: the normalized flow-off intensity drops by ∼27%, and the flow-induced change is reduced to ∼+5% ($I_{FlowOff}$ = 0.73, I_{FlowOn} = 0.76). As the following explanation shows, both effects can be conceptually understood by charge screening. The increase in ionic strength I by two orders of magnitude (i.e., from 1 to 100 mM) decreases the surface potential Φ_0 according to eq 2. Due to the correlation between Φ_0 and the v-SFG intensity (eq 1), the v-SFG intensity decreases as well. We note that decreases in the v-SFG response have been observed previously for the fluorite-water[8] and the silica-water[11] interfaces. Equations 1 and 2 are also instructive in understanding the less pronounced changes upon flow. Due to the increased ionic strength, the same change in surface charge (upon flow) will be less reflected by the surface potential and, thus, the overall v-SFG intensity. Hence to explain the results, it suffices that the interaction of sodium chloride with the charged fluorite surface is limited to screening the surface charge. Note that the ionic strength is hardly changing upon flow as only the concentration of the dissolved ions (<1 mM) decreases due to flow-induced dilution. If the effects of all salts would just be screening, one expects to see the same effects with the same

magnitude upon varying the type of salt but keeping the concentration the same.

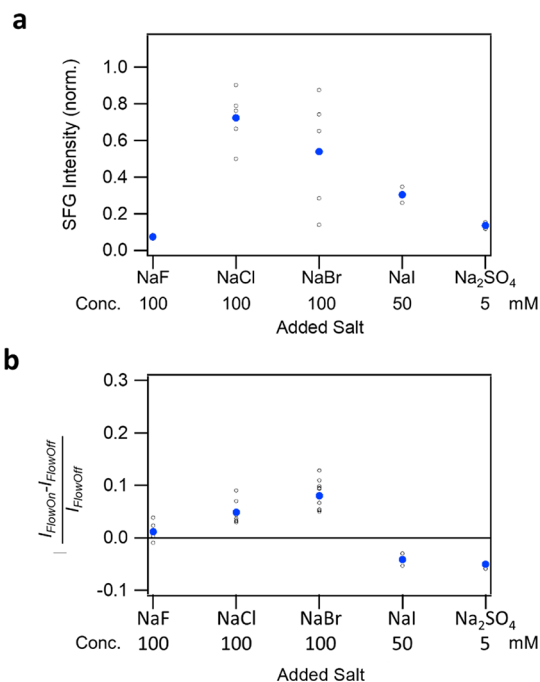To test this hypothesis, we show in Figure 2 how the exchange of anions affects the v-SFG experiments. High

Figure 2. Anion-specific interaction at the fluorite-water interface. (a) Flow-off v-SFG intensities at the fluorite-water interface at 1 mM HCl with the addition of the indicated salts. The intensities are normalized to the one obtained with bare 1 mM HCl solution. The filled circles represent averages over several experiments, while the open circles represent the spread of the single experiments. The added salts are listed on the x-axis with the concentration in mM underneath. (b) Relative change in the v-SFG intensity upon flow at the fluorite-water interface with the same solutions used in (a). The relative change is calculated based on averaging the level of the flow-off and flow-on intensity over the last minute before changing the flow state. Such levels are marked in Figure 1b. All data are listed in the tabular form in the SI (Table S2).

amounts of fluoride lead to the lowest v-SFG intensity, significantly lower than the addition of NaCl, and to no significant change upon flow (see also Figure S3 in the SI), which has also been observed in previous studies.[17−19] Based on the explanation for the addition of sodium chloride, we can conclude that the interaction between fluoride anions and the fluorite surface goes beyond charge screening, which is consistent with fluoride adsorption as the interaction currently accepted in the literature. Due to the excess of fluoride anions, adsorption of this ion is saturated, leading to low surface charges and a correspondingly small v-SFG response. The presence of fluoride in the bulk solution also suppresses dissolution, which is why hardly any concentration change upon flow occurs. Thus, the v-SFG intensity is unaffected by the presence of liquid flow. The concentration used in this study is higher than that in previous ones and therefore shows that the effect of no flow-induced change persists at increasing fluoride concentrations, which corroborates the explanation of adsorption.

On the other hand, adding bromide instead of fluoride has a qualitatively similar although quantitatively different effect as

adding chloride. The magnitude of the v-SFG intensity is around 50% of that of the bare 1 mM HCl solution but with a large error bar, and the flow-induced change is around ~+10%. Overall, similar surface potentials and interfacial chemistry are likely occurring when adding sodium chloride and bromide, thus pointing to screening as the main interaction between ion and surface, with the screening being somewhat ion-specific, leading to the quantitative differences. The reason for the similarity is that both chloride and bromide anions are, unlike fluoride, not part of the CaF_2 crystal and therefore do not affect the adsorption/desorption equilibria, which could be viewed as the dissolution/precipitation of the crystal's ions at the surface. Precipitation of chloride and bromide is unlikely as the ionic radius is different from the ionic radius of fluoride and thus not "fitting" in the crystal lattice. The same argument holds for the flow-induced changes, as they are connected to a change in concentration of dissolved ions, not being affected by the addition of chloride and bromide. In contrast, the addition of iodide and sulfate salts affects the interfacial chemistry differently. Both those anions lead to relatively small v-SFG intensities. Note that for those salts, the added concentration was even reduced to 50 and 5 mM in the case of sodium iodide and sodium sulfate, respectively. Those concentrations are shown since they gave rise to the interesting observation of flow-induced decreases in the v-SFG intensity, which do not occur at elevated concentrations, as shown in Figure S1 of the Supporting Information. When comparing sodium iodide and fluoride at 100 mM, they affect the v-SFG intensity and its change upon flow very similarly. However, it is the observation of the flow-induced decrease that is the key observation for the following discussion.

Although the iodide anion, like chloride and bromide, is not part of the CaF_2 crystal, it exhibits a different surface chemistry. We propose that this can be explained by the high surface affinity, similar to that at the water-air interface, as it is repelled from the hydrogen-bonded water network due to its large size, low charge density, and high polarizability.[21,22] Therefore, a more direct interaction with the fluorite surface is likely. We propose that iodide, like fluoride, adsorbs. Accordingly, the reaction from eq 3 can be generalized to the reaction from eq 6, where X represents an adsorbing anion, like fluoride or iodide. The excess of iodide shifts the equilibrium of eq 6 to the left side with lower surface charge, which explains the lower magnitude of the v-SFG intensity compared to not adsorbing anions like chloride. Iodide adsorption can also explain the reversed sign in the flow-induced change, i.e., the intensity decrease upon flow. Due to the excess of adsorbing anions, the dilution of dissolved fluoride anions upon flow becomes negligible. This has also been shown recently by varying the added amount of fluoride.[17] With an excess of adsorbing anions (here X = I), the equilibrium from eq 5 does not change upon flow. What is changing upon flow, however, is the adsorption equilibrium of dissolved calcium ions from reaction 4. The reduced concentration there leads to less adsorption and correspondingly lower surface charges and v-SFG intensities upon flow. This explanation is further supported by a control experiment, where we added some calcium to the iodide solution (Figure 3). This addition suppresses the dilution of calcium upon flow, resulting in the absence of a flow-induced change.
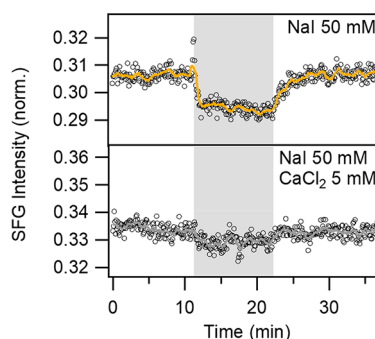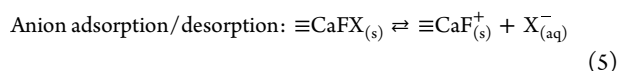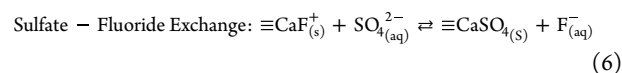
$$\text{Anion adsorption/desorption: } \equiv CaFX_{(s)} \rightleftarrows \equiv CaF_{(s)}^{+} + X_{(aq)}^{-}$$

$$(5)$$

Figure 3. Interplay of iodide and calcium adsorption V-SFG intensity development during a flow-on/off cycle. The flow-on region is highlighted in gray. The open black circles represent integrated spectra, and the colored solid lines are ten-point moving averages to guide the eye. The top panel shows the intensities of the flow experiment conducted at a 1 mM HCl solution with 50 mM NaI added, while the bottom panel shows the data for a similar solution additionally containing 5 mM $CaCl_2$. The v-SFG intensities under flow-off conditions are normalized as shown in Figure 2a.

For sulfate, already at 5 mM concentrations, a flow-induced decrease in the v-SFG intensity is also observed. Sulfate is a divalent anion, which is expected to have a greater influence of adsorption to the surface, in line with the magnitude of the v-SFG intensity being lower than the one of iodide, even though sulfate is present in a ten times lower concentration (Figure 2). Additionally, the divalent nature of sulfate let us speculate about an additional adsorption mechanism, which is a fluoride-sulfate exchange (eq 6). Not only is such a reaction in line with the more reduced surface potential (and v-SFG intensity) compared to iodide but it also serves as an additional and intuitive explanation of the flow-induced changes: Upon flow-induced dilution, the fluoride concentration decreases, driving the equilibrium from eq 6 to the right side and thereby lowering the surface charge as observed by a flow-induced decrease of the v-SFG intensity. This adsorption mechanism might be further supported by the change in the spectral shape, as discussed in S3 of the SI.

$$\text{Sulfate} - \text{Fluoride Exchange: } \equiv CaF_{(s)}^{+} + SO_{4(aq)}^{2-} \rightleftarrows \equiv CaSO_{4(S)} + F_{(aq)}^{-}$$

$$(6)$$

Besides the anion-specific effects, we also studied the influence of different cations. However, as fluorite exhibits a positive surface charge under the investigated conditions, no effect of changing the cation is expected. This is true for most of the studied cations, as apparent from Figure 4, which summarizes the normalized v-SFG intensities and their relative changes upon flow upon adding various chloride salts. All added salts give rise to similar v-SFG intensities somewhat smaller than that of the bare 1 mM HCl solution, to which the intensities are normalized. As discussed for sodium chloride, this can conceptually be understood from charge screening with comparable surface potentials. Interestingly, we observe that the flow-induced changes reveal that the interfacial chemistry must be affected in a cation-specific manner, although the surface is positively charged. Lithium, sodium, and potassium chloride show very similar flow-induced changes. The one of cesium chloride, however, is more than two times higher but does not lead us to assume that there is an effect that qualitatively differs from charge screening. We rather propose that, as in the case of bromide, the observations
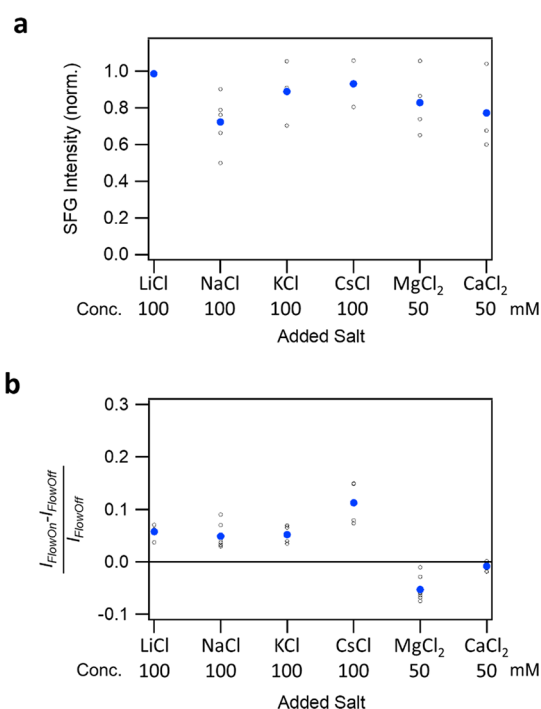
Figure 4. Cation-specific interactions at the fluorite-water interface. (a) Flow-off v-SFG intensities at the fluorite-water interface at 1 mM HCl with the addition of the indicated salts. The intensities are normalized to the one obtained with a bare 1 mM HCl solution. The filled circles represent averages over several experiments, while the open circles represent the spread of the single experiments. The added salts are listed on the x-axis with the concentration in mM underneath. (b) Relative change in the v-SFG intensity upon flow at the fluorite-water interface with the same solutions used in (a). The relative change is calculated based on averaging the level of the flow-off and flow-on intensity over the last minute before changing the flow state. Such levels are marked in Figure 1b. All data are listed in tabular form in the SI (Table S2).

point to ion-specific variations in charge screening. Even more specific events come into play with the addition of 50 mM calcium and magnesium. With the addition of calcium, no changes appear upon flow. As for the addition of calcium, this appears reasonable since, like with the addition of fluoride, dissolution of the mineral is suppressed. Consequently, there is hardly any dilution upon flow and no change in the surface potential and the corresponding v-SFG intensity. Unlike fluoride addition, however, the addition of calcium does not lead to saturation in adsorbed anions and thus does not reduce the surface potentials. As a result, the SFG signal is in the same order of magnitude as for the addition of NaCl. Interestingly, the addition of magnesium also triggers a flow-induced decrease in the v-SFG intensity. We assume that a more complex interaction between magnesium cations and the fluorite surface is present. For sure, the effects observed for the magnesium cation go beyond charge screening, which could not explain a flow-induced decrease. We suppose that the effect could be connected to an interaction of magnesium with the dissolved ions close at the interface. While the details of such a mechanism are speculative for now, we hope that it promotes future research and are convinced that our flow experiments add information to the discussion of ion-specific interactions that are not accessible from the magnitude of v-SFG intensity under static conditions only. We hope that our observations

and interpretations promote the usage of surface-sensitive spectroscopy combined with flow but also trigger further research, including simulations on the interfacial chemistry at mineral-water interfaces.

■ CONCLUSIONS

In this study, we used surface-specific v-SFG spectroscopy and the change in the concentration of dissolved ions that appear upon flow-induced dilution to investigate ion-specific interactions at the charged fluorite-water interface. We find that the interaction of many salts is limited to charge screening with minor variations in the precise surface potential. However, we also find adsorption as a more direct interaction for certain anions as iodide and sulfate. More complex interactions are suggested by our observations with magnesium cations in the aqueous phase. While not all details are resolved yet, it is clear that following the v-SFG intensity during a flow experiment adds valuable information inaccessible from static experiments and that needs to be considered to adequately describe how ions specifically affect the interfacial chemistry at a mineral-water interface.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c01789.

Specifications of the chemicals and additional SFG data for sodium sulfate and sodium iodide (PDF)

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Author Contributions

P.O., E.H.G.B., and M.B. designed the research project. P.O. and S.H.K. performed the experiments and P.O. analyzed the data. All authors discussed the results and wrote the manuscript.

Notes

The authors declare no competing financial interest.

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