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Calcium fluoride is a slightly soluble compound commonly extracted from ores via flotation at elevated pH, where surfactant molecules bind with hydroxylated surface sites. The addition of F⁻(aq) suppresses surfactant adsorption by replacing these sites. In this paper, we look at the effects of aqueous Cl⁻, Br⁻, F⁻, and SO₄²⁻ on the water structure at the CaF₂/H₂O interface at a pH where surface hydroxylation has not yet occurred. Using static and time-resolved vibrational sum-frequency spectroscopy (VSFS), we find that aqueous Cl⁻ and Br⁻ have only electrostatic screening effects on the interface and do not perturb the interfacial water or surface structure. Sulfate, which we find to be strongly attracted to the interface, affects the interfacial water more than Cl⁻ or Br⁻. This is in contrast to F⁻ ions that directly interact with the surface and alter the water structure and bonding at the CaF₂ surface in addition to screening the surface charge.

Introduction

The charged solid/aqueous interface is of great importance in a variety of processes, both natural and industrial, and therefore has been the subject of much interest. Processing of mineral ores typically uses chemical flotation, which is dependent on surface chemical properties that are influenced by the dissolution of the surface ions.¹ Commonly these interfaces are investigated through spectroscopic^{2,3} or electrokinetic^{4,5} methods requiring the use of fine powders; however, the random orientation of the crystallographic planes of the powders and the high defect density can yield significantly different results compared to planar crystalline surfaces. For example, the isoelectric point (IEP) of alumina has been reported as pH 5.5 for a single crystal surface and pH 9 for powders.⁶ Accessing these interfaces can be done spectroscopically, but interfacial behavior that occurs at the water–salt interface is often difficult to distinguish from the larger effects of the bulk aqueous solution. Vibrational sum-frequency spectroscopy (VSFS), which is used in the studies herein, is ideally suited to these types of studies because it is inherently sensitive to the small number of interfacial species present without regard to those in the bulk phase.

There has been much effort devoted to understanding interactions of adsorbates at the fluorite/water interface. An array of

sulfate and carboxylate surfactants adsorbing at this interface have been studied in this laboratory^{7–15} and others^{16–19} using both static and dynamic measurements. These studies have found that adsorption processes occur at the interface via interaction with hydroxyl-substituted sites, based on the increase in adsorption with increasing pH. Direct spectroscopic evidence for the presence of surface hydroxyls at pH 6.4 and higher has been reported.⁷ A recent study by Schrödle et al. examined acetate adsorption at the CaF₂/water interface.¹² It found that acetate adsorption increases with increasing pH but is strongly suppressed by F⁻ ions added in excess of the solution equilibrium concentration predicted by the CaF₂ solubility equilibrium constant. The authors concluded that F⁻ replaces significant numbers of surface hydroxyls, which are present at pHs greater than the point of charge neutrality (pH ≈ 8.5), reducing the number of surface binding sites where acetate can adsorb. This finding was unexpected given that zeta-potential measurements have not found F⁻ to be a potential determining ion for CaF₂, suggesting that F⁻ is not able to directly interact with the CaF₂ surface.^{4,20–23} These studies proposed that breaking of the tightly held solvation shell of F⁻ was not sufficiently energetically favorable to allow the ion to penetrate the hydration layer of the fluorite surface and bind with the surface.

To reconcile these results, the study within directly interrogates the CaF₂/water interface with VSFS using aqueous F⁻, Cl⁻, Br⁻,

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SO_4^{2-} , and Ca^{2+} ions. These studies are conducted at a constant pH that is slightly below the point of charge neutrality, in nonequilibrium conditions maintained using a constant flow of solution over the surface. Use of flowing solutions replicates conditions commonly used in electrokinetic measurements of interfacial potentials while retaining the sensitivity advantages of nonlinear spectroscopy by directly measuring the interfacial structure, not the potential at the shear plane, some distance beyond the electric double layer. The selected pH ensures that the surface has a small, net positive charge but is free of hydroxyl-substituted sites that may preferentially interact with the introduced ions. Using a combination of static and dynamic studies, we show new information regarding the direct interaction of F^- and the very different behavior of the other ions with the CaF_2 surface and surrounding interfacial water molecules.

VSFS Background

The theory and fundamental concepts of VSFS has been extensively discussed;^{24–28} briefly, VSFS is a second-order nonlinear optical technique in which a fixed frequency visible beam (ω_{vis}), far from electronic resonance with the species present, and a tunable IR beam (ω_{IR}) are overlapped in space and time at the interface between different media. The molecules in the interfacial region, which is a noncentrosymmetric environment, interact with the incident fields and generate a new field that oscillates at the sum of the incident frequencies (ω_{SF}). When the IR frequency samples a vibrational resonance, the VSFS signal is enhanced, which results in an interfacial vibrational spectrum. For this study, all spectra were obtained using the SSP polarization scheme which probes vibrational modes with dipole components perpendicular to the interface.

Detailed analysis of VSF spectra requires nonlinear curve fitting of the data. The detected VSF signal $I(\omega_{\text{SF}})$ is given by eq 1

$$I(\omega_{\text{SF}}) \propto |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{IR}}) I(\omega_{\text{vis}}) \quad (1)$$

where $I(\omega_{\text{IR}})$ and $I(\omega_{\text{vis}})$ are the intensities of the incident infrared and visible beams, respectively, and $\chi_{\text{eff}}^{(2)}$ is the macroscopic nonlinear susceptibility. $\chi_{\text{eff}}^{(2)}$ is composed of a nonresonant $\chi_{\text{NR}}^{(2)}$ component and a resonant contribution from the i th vibrational mode $\chi_{v_i}^{(2)}$. These resonant modes are fitted to eq 2

$$\chi_{v_i}^{(2)} = A_i e^{i\phi_i} \int_0^\infty \frac{1}{\omega_{v_i} - \omega_{\text{IR}} + i\Gamma_{L_{v_i}}} e^{(-\omega_{v_i} - \omega_{\text{IR}})/\Gamma_{v_i}} dt \quad (2)$$

where A_i , ϕ_i , ω_{v_i} , $\Gamma_{L_{v_i}}$, and Γ_{v_i} are fittable parameters for the amplitude, phase, resonant frequency, Lorentzian line width, and Gaussian line width of the i th mode. A global fitting routine in IgorPro (Wavemetrics, Beaverton, OR) was used to analyze all spectra within a concentration series simultaneously.

Experimental Section

Details of both the laser system²⁹ and experimental setup⁷ have been previously reported. The experiments described within utilize a commercially available laser and IR generation stage

(Ekspla) producing 532 nm pulses and tunable IR (2700–3900 cm^{-1} for this experiment). The visible and IR beams were incident on a 68° CaF_2 prism in a total internal reflection geometry with incident angles 20.5° and 17° from horizontal, respectively. All frequency domain spectra were collected at 4 cm^{-1} resolution, 60 shots per data point. The time-resolved experiments were performed averaging 60 shots per point with an acquisition rate of approximately 1 point per 16 s. The resulting VSF signal was filtered by narrow bandpass filters and detected with a monochromator attached photomultiplier tube. This signal was then normalized to both the visible and IR energy.

The solutions in contact with the prism were constantly flowing by means of a peristaltic pump connected to a Kel-F cell via PTFE tubing. This was critical to prevent dissolution of the CaF_2 from affecting the pH of the unbuffered solutions. The cell has a height of 2.5 mm with a volume of 0.15 mL. The flow rate used in these experiments, ≈ 1 mL/min, replaces the contents of the cell six to seven times a minute, a time scale much longer than the diffusion of ions to the interface. The solution reservoir was continually monitored by a glass electrode connected to a calibrated pH meter.

The NaCl and NaBr salt solutions were made from 10 M ionic strength stock via serial dilution with H_2O (resistivity ≈ 18.2 $\text{M}\Omega \cdot \text{cm}$) and NaF, Na_2SO_4 , and CaCl_2 from 1 M ionic strength stock solutions. The salt solutions were all adjusted to $\text{pH } 5.8 \pm 0.2$ via small additions of HCl or NaOH as needed and continually flowed over the surface. The salts were purchased from Aldrich (SigmaUltra) and baked at 250 °C overnight prior to use. All glassware was cleaned by soaking in concentrated sulfuric acid with NoChromix (Godax Laboratories) and rinsing with copious amounts of purified water. The surface of the CaF_2 prism was regularly cleaned by briefly soaking in sulfuric acid, polishing with 0.05 μm Al_2O_3 powder and rinsing with purified water.

Results and Discussion

A. Solution Equilibrium Structure. Upon exposure of CaF_2 to water at pH 5.8, preferential dissolution of the fluoride ions generates a positive interfacial potential. This potential results in the orientation of water molecules in the interfacial region with their dipoles normal to the surface, as measured in these VSF experiments. These electrostatically oriented molecules occupy the electric double layer. This region defines the optically probed interface and has a thickness that varies with ionic strength and surface charge. VSFS has previously been used to investigate the effects of pH on this interface.⁷ As the pH approaches the pH of the point of zero charge, the VSF signal from the molecules in the double layer decreases due to decreasing surface charge. To probe ion specific effects, the pH is held constant at 5.8, keeping the surface charge constant, and electrolytes of varying concentrations are introduced into the cell. The VSF spectra have been recorded for different concentrations of various electrolytes (see Figure 1). As ions are introduced to the interfacial region, the positive surface charge is screened. Using the Gouy–Chapman model, which has been shown to accurately characterize the interfacial potential for solid/electrolyte systems,^{30,31} we can understand the degree of this screening behavior. The Debye–Hückle length, or thickness of the double layer, can be readily calculated for CaF_2 .³² On the basis of the solubility equilibrium constant of CaF_2 , which gives an equilibrium ionic strength of 9.9×10^{-4} M, this depth is 9.7 nm and is decreased to 9.6 Å by a 0.1 M ionic strength solution. The compression of the

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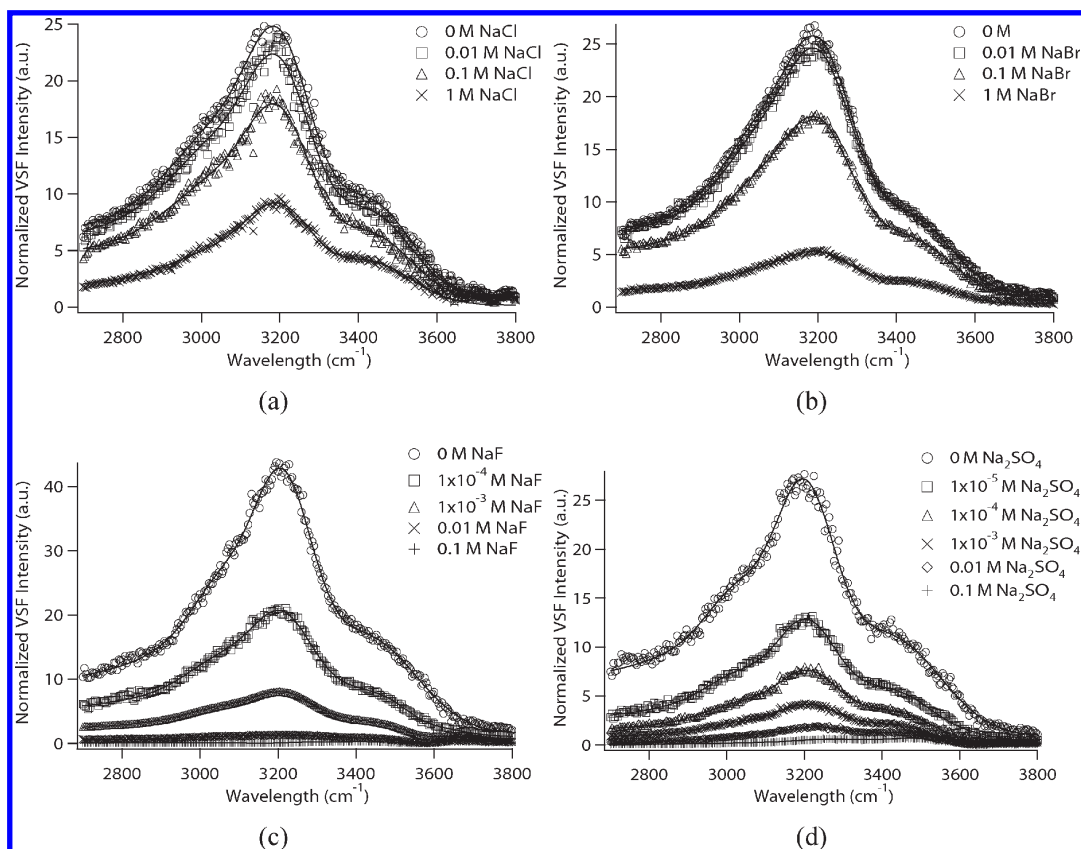


Figure 1. Concentration series VSF spectra for (a) NaCl, (b) NaBr, (c) NaF, and (d) Na_2SO_4 . The data for 0.1 M NaF and 0.1 M Na_2SO_4 are shown on an expanded scale in Figure 2.

double-layer region reduces the number of electrostatically oriented interfacial water molecules, resulting in a smaller VSF signal in this spectral region. As a consequence, water molecules most closely interacting with the surface are revealed.

Recent results from Miller et al.²² found the potential of a flat CaF_2 (111) surface to be negative at pH 5.8, which would appear to be in conflict with our previous VSF studies.^{7–15} However, the crystallographic orientation has a significant effect on the surface charge. The isoelectric point of a (110) CaF_2 plate was recently measured by atomic force microscopy, which found the surface to be positively charged below pH 9.2. The results presented here are collected on an amorphous CaF_2 prism, which bears more similarity to the commonly used powdered CaF_2 used in traditional zeta-potential measurements. These measurements have long found that CaF_2 at this pH is positively charged.^{21,22,33,34}

Neat CaF_2 /water spectra are shown in all four panels of Figure 1 as the \circ marked spectra. The spectra for all the solutions show the same general features with a large broad peak centered around 3200 cm^{-1} . This spectral region corresponds to water molecules with relatively strong bonding interactions whereas spectral features at higher frequencies ($3400\text{--}3700\text{ cm}^{-1}$) represent interfacial water molecules with weaker hydrogen-bonding interactions. To facilitate the comparison of changes in spectral regions for different electrolyte containing solutions, we employ spectral fitting routines that deconvolute the overall spectral envelope into several spectral regions.^{35,36} The results for the

contributing peaks found from the best fits to the CaF_2 /water spectra are shown in Table 1. The differences between the fit parameters for these water spectra are primarily due to variations of the prism surface between polishes which change the VSFS spectra slightly. Because of the broadness of the reported peaks, the differences in location and amplitude are not significant.

Figure 1a shows the VSF spectra of the CaF_2 /NaCl(aq) interface as a function of ionic strength. Changes in the water spectrum were not appreciable for concentrations less than 0.001 M ionic strength. At $I = 0.01\text{ M}$, a decrease in the VSF intensity over the whole spectral region was observed. This indicates that the predominant coordination environments at ~ 3050 , ~ 3225 , and $\sim 3450\text{ cm}^{-1}$ are equally affected by the presence of ions near the interface. The $\text{Cl}^{\text{-(aq)}}$ anions are not particularly effective at screening the charge near the surface or altering the hydrogen-bonding network, as the spectral intensity remains strong and both the locations and relative intensities of the spectral regions representing the different coordination environments remain unchanged at $I = 1\text{ M}$. Even though both $\text{Na}^{\text{(aq)}}$ and $\text{Cl}^{\text{(aq)}}$ are considered weakly hydrated ions, the ions do not appear to form a counterion layer close to the charged CaF_2 surface that would significantly screen the surface charge, resulting in a lower water signal, and disrupt the hydrogen-bonding network of the interfacial water molecules.

The NaBr solution spectra in Figure 1b show similar behavior at the CaF_2 surface compared to NaCl solutions. The spectra were fit to three broad peaks of constant location and width (3060 , 3231 , and 3459 cm^{-1}), all of which decrease in amplitude with increasing Br^- concentration. Differences between Br^- and Cl^- ion containing solution are negligible until 1 M ionic strength, at which point Br^- decreases the VSF signal significantly more than Cl^- . For the three water peaks, the average peak amplitude

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Table 1. Spectral Fitting Parameters for Water and Salt Solutions of the Following Ionic Strengths: $I(\text{NaCl}) = 1 \text{ M}$, $I(\text{NaBr}) = 1 \text{ M}$, $I(\text{Na}_2\text{SO}_4) = 0.1 \text{ M}$, $I(\text{NaF}) = 0.1 \text{ M}$, and $I(\text{CaCl}_2) = 1 \text{ M}$ ^a

salt	water spectra parameters			highest concentration parameters		
	location (cm^{-1})	width (cm^{-1})	amplitude	location (cm^{-1})	width (cm^{-1})	amplitude
NaCl	3059 ± 1	135 ± 2	0.93 ± 0.03	3059 ± 1	135 ± 2	0.54 ± 0.05
	3227 ± 1	114 ± 1	2.96 ± 0.02	3227 ± 1	114 ± 1	1.94 ± 0.04
	3447 ± 1	157 ± 1	2.09 ± 0.02	3447 ± 1	157 ± 1	1.55 ± 0.03
NaBr	3060 ± 1	104 ± 2	0.66 ± 0.02	3060 ± 1	104 ± 2	0.24 ± 0.03
	3232 ± 1	124 ± 1	3.14 ± 0.01	3232 ± 1	124 ± 1	1.30 ± 0.03
	3459 ± 1	159 ± 1	1.83 ± 0.02	3459 ± 1	159 ± 1	1.00 ± 0.02
Na ₂ SO ₄	3039 ± 2	87 ± 2	0.69 ± 0.02	3056 ± 15	76 ± 11	0.07 ± 0.02
	3229 ± 1	115 ± 1	2.99 ± 0.01	3254 ± 5	86 ± 12	0.20 ± 0.02
	3456 ± 1	178 ± 1	2.33 ± 0.02	3483 ± 1	258 ± 1	0.82 ± 0.02
NaF	3078 ± 3	102 ± 5	0.96 ± 0.11	3615 ± 3	75 ± 5	-0.48 ± 0.03
	3239 ± 6	104 ± 2	3.45 ± 0.09	3225 ± 4	62 ± 5	-0.15 ± 0.01
	3449 ± 5	204 ± 10	2.9 ± 0.1	3464 ± 5	88 ± 3	0.31 ± 0.01
CaCl ₂	3039 ± 2	86 ± 3	1.03 ± 0.04	3622 ± 2	52 ± 2	-0.64 ± 0.01
	3216 ± 1	110 ± 1	3.77 ± 0.08	3090 ± 8	76 ± 11	0.20 ± 0.02
	3417 ± 1	147 ± 1	2.4 ± 0.1	3234 ± 2	80 ± 3	0.72 ± 0.02
				3483 ± 1	258 ± 1	0.82 ± 0.02
				3671 ± 5	120 ± 11	0.27 ± 0.02

^a Negative and positive amplitudes correspond to phases of π and 0, respectively. The reported errors are those of the spectral fits.

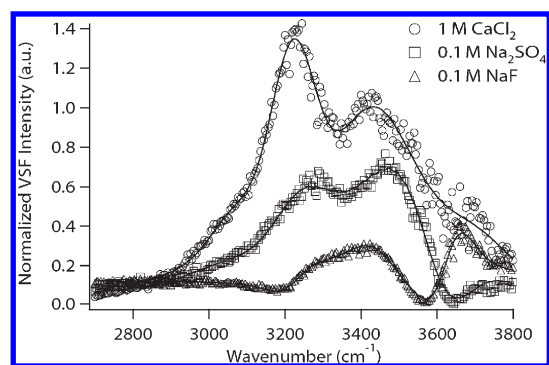


Figure 2. VSF spectra of 0.1 M NaF (Δ), 0.1 M Na₂SO₄ (\circ), and 1 M CaCl₂ (\square) solutions which show significant deviations from neat water spectra. These spectra demonstrate differences in spectral features and have not been normalized to each other.

decrease is 20% more for 1 M NaBr relative to 1 M NaCl. A likely explanation for this is the greater polarizability of Br⁻ compared to Cl⁻. The greater size of Br⁻ allows it to be more readily distorted by the surface electric field than Cl⁻, resulting in a larger induced dipole, which may increase surface attraction. However, the Br⁻ ions also do not appear to form dense counterion layers in the interface, as there is only a small decrease in VSF signal at 0.1 M ionic strength and no significant changes in the best fit parameters, which would represent a change in the interfacial bonding environment.

The final monatomic ion examined was fluoride. The addition of F⁻ to the CaF₂/H₂O interface results in distinctly different changes in the interfacial water spectra compared to Cl⁻ and Br⁻. The interfacial water, as manifested in the VSF intensity, is far more sensitive to the presence of added F⁻ than either Cl⁻ or Br⁻. Plots of the spectra in Figure 1c clearly show changes with concentration. First, spectral intensity begins to decrease at $1 \times 10^{-4} \text{ M}$, which is 2 orders of magnitude lower than for Cl⁻ or Br⁻. Second, the overall shapes of the spectra change with increasing ionic strength. By 0.1 M ionic strength, which is shown in Figure 2 for clarity, the spectrum is quite different from the neat H₂O/CaF₂ spectrum shown in Figure 1c. At low concentrations, the spectra can be described by three broad modes representing a range of coordination environments which are similar to those seen in the Cl⁻ and Br⁻ containing spectra. As the concentration is increased

to 0.1 M, ions populate the interfacial region, further screening the surface charge, altering the hydrogen-bonding network, which can be seen by the differences in the fit parameters of water and 0.1 M NaF in Table 1. The result is a decrease in VSF amplitude throughout the spectral region studied, with the largest intensity now coming from water molecules much more loosely coordinated. This behavior is clearly different from the other ions studied. This demonstrates that at these high concentrations of F⁻ the interfacial water is significantly perturbed throughout the interfacial region by F⁻-H₂O interactions that alter and weaken the H₂O-H₂O and H₂O-CaF₂ interactions. The best fit to the spectrum for 0.1 M NaF results in three peaks at 3225, 3464, and 3622 cm⁻¹. The 3622 cm⁻¹ peak appears at concentrations as low as 1 mM, and its amplitude increases with increasing concentration. The phase of this peak is consistently opposite that of the coordinated water environments, as shown by the negative sign in front of the amplitude in Table 1. Because of this amplitude increase and the peak location, we attribute this mode to water molecules solvating F⁻ ions in the interfacial region. The phase difference between this mode and the coordinated water envelope reflects the orientation differences between water hydrating the positively charged CaF₂ surface and the negatively charged ion. This charge difference causes the direction of the water dipoles to be oppositely oriented in the two environments. Fluoride ions are known to be strongly hydrated; the reported enthalpy of solvation of F⁻ is $\sim 510 \text{ kJ/mol}$, which is significantly higher than Cl⁻ or Br⁻.³⁷ Ion solvating water molecules are commonly found in this spectral region by VSFS and are likely due to induced asymmetry in the solvation shell of the ion as it nears the charged surface.^{10,38,39} The small peak at 3225 cm⁻¹ is unique to the highest concentration tested. We attribute this peak to water molecules hydrogen bonding with surface bound F⁻ ions which create local charge environments different from that of the surface overall. Microsolvation studies support these conclusions, with F⁻/H₂O hydrogen bonds having been seen near 3200 cm⁻¹ and inter-water hydrogen bonds of the ion solvation shell near 3600 cm⁻¹.^{40,41}

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Either or both of these species are likely present in the interface at lower concentrations than seen in our spectra, but they are masked at the lower concentrations where water molecules in the double-layer region dominate the spectrum of those molecules closest to the CaF_2 surface. This is not unexpected as the solvated ion effect should be weak. On the basis of Gouy–Chapman theory, the charge density of the diffuse layer is 0.0061 C/m^2 and that of a F^- ion is 0.721 C/m^2 ;⁴² thus, solvated ions must be very close to the interfacial plane for there to be sufficient symmetry breaking to generate a signal, and that signal will be weak relative to that of the electrically oriented water in the double layer.

Sulfate ions were also examined at this interface. Sulfate ions in the aqueous phase provide an interesting comparison to the other anions studied here because of their divalent character, which should lead to stronger surface bonding at the positively charged aqueous CaF_2 surface and a tendency to form robust solvation shells.³⁷ Presented in Figure 1d are VSF spectra that show SO_4^{2-} affects the interface at concentrations as low as $1 \times 10^{-5} \text{ M}$ by a large decrease in VSF signal. Compared to the monovalent ions, and in particular NaCl(aq) , SO_4^{2-} ions much more effectively screen the surface charge; i.e., they have a high tendency to be located close to the interface even at low concentrations. Additionally, every SO_4^{2-} ion adsorbed at the interface compensates two positive charges and is thus able to reduce the interfacial field more than Cl^- . With regards to spectral fitting, the VSF spectra of the Na_2SO_4 solutions show a smooth shift in fitted frequency from the values of the $\text{CaF}_2/\text{H}_2\text{O}$ spectrum to those of the $I = 0.1 \text{ M Na}_2\text{SO}_4(\text{aq})/\text{CaF}_2$ spectrum in Table 1. The fitting results describing the broad vibrational modes of the coordinated water environment of the highest concentration spectrum are 3056 , 3554 , and 3483 cm^{-1} . These values are slightly higher than the initial values of the pure water spectrum. This is consistent with a weakening of the $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions due to the more disruptive nature of the SO_4^{2-} ions that are larger and have larger solvation shells than Cl^- or Br^- . As a comparison, the enthalpies of solvation of SO_4^{2-} , Cl^- , and Br^- are -1018 , -336 , and -367 kJ/mol , respectively.³⁷ Evidence for these solvating water molecules near the surface can be found in the spectra near 3600 cm^{-1} , where significant spectral changes occur at the higher concentrations that reveal interactions closer to the surface. To account for these changes, it is necessary to add a small peak with a phase opposite that of the coordinated water regions at 3597 cm^{-1} to improve the overall fit. Water molecules solvating the ionized headgroup of sodium dodecyl sulfate at the $\text{CaF}_2/\text{H}_2\text{O}$ interface have previously been seen near the same location by VFS.¹⁰

To study the effect of the Ca^{2+} ion, which is always present in the aqueous phase due to the solubility equilibrium of CaF_2 , CaCl_2 solutions were also examined. While they have minimal effect on bulk pH, Ca^{2+} ions have been shown to affect the zeta-potential of CaF_2 .²² This means that the ions can directly interact with the surface by adding to the fluorite lattice. Because of the positive charge of the surface and the weak interaction of Cl^- ions at the interface, very little effect on the VSF spectra can be seen until 0.01 M ionic strength (see Supporting Information). The parameters of the peaks used are shown in Table 1 and are similar to those used for the other spectra presented here. Unlike the F^- ion spectra, there is no apparent shifting of the spectral resonances with the addition of CaCl_2 until 1 M ionic strength is reached, shown in Figure 2. At this point, it becomes clear that an additional broad peak is required to fit the spectra at 3672 cm^{-1} . We attribute

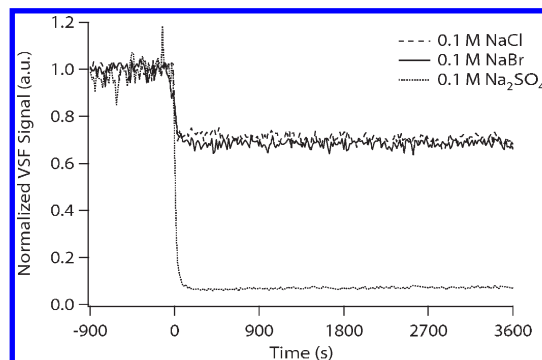


Figure 3. VSF signal at 3200 cm^{-1} monitored over time for NaBr , NaCl , and Na_2SO_4 at the $\text{CaF}_2/\text{water}$ interface. The data values are all normalized to 1 prior to the introduction of the salt solutions, and time = 0 corresponds to the beginning of signal decay.

this peak to water molecules hydrating Ca^{2+} ions because the phase of this peak is opposite that of the solvation peak in the F^- and SO_4^{2-} ion spectra due to the positive charge of the ion. Furthermore, this frequency is close to that found for Ca^{2+} ions in infrared action spectroscopy.⁴³

B. Ion Kinetics at the $\text{CaF}_2/\text{Water}$ Interface. To augment the insights gained from the spectroscopic experiments, time-resolved studies were performed that monitor the change in spectral intensity as a function of time after the addition of the different salts discussed previously. Two wavelengths were measured simultaneously, before and after introduction of the salt solution. The first frequency probed was 3200 cm^{-1} , which probes the strongly coordinated water molecules in the double layer and also those hydrating the surface. The second frequency chosen was 3590 cm^{-1} , which measures more weakly hydrogen-bonded species including ion solvating water molecules. The VSF signal CaF_2 surface was initially allowed to stabilize with water, after which the desired salt solution was pumped into the cell and monitored until the signal no longer changed. Figure 3 shows the time-resolved VSF signal for 0.1 M Cl^- , Br^- , and SO_4^{2-} with the initial water signals all normalized to one. All traces show a rapid drop in intensity, on the order of a few seconds, as soon as the salt solution is introduced into the cell at time = 0 s. As the ions populate the interfacial region of the charged CaF_2 surface, the number of interfacial water molecules contributing to the spectral response is reduced due to screening of the interfacial potential as the ions diffuse to the interface. Beyond the rapid decrease for Cl^- , Br^- , and SO_4^{2-} , the VSF response remains relatively constant for the duration of the experiment. The traces at 3590 cm^{-1} (see Supporting Information) show identical kinetics, even for the SO_4^{2-} ion, showing that the population of the solvated species tracks with the decrease in the number of water molecules.

For moderately and highly concentrated solutions of NaF , different results are obtained as shown in Figure 4. Initially, a fast drop in intensity is observed at both frequencies, similar to the other ions. However, this sharp decline is followed by a decrease in VSF signal that takes about $1800\text{--}3600 \text{ s}$, which can be seen most clearly in the 0.1 M traces for both wavelengths. The similarity in the intermediate decays at these two frequencies at high concentrations indicates the changes in the interfacial water in this time frame are at least influenced by the same interfacial process and possibly originate from the same source. Previous electrochemical and spectroscopic studies have made note of long time scale (tens of hours) instability for fluorite/water

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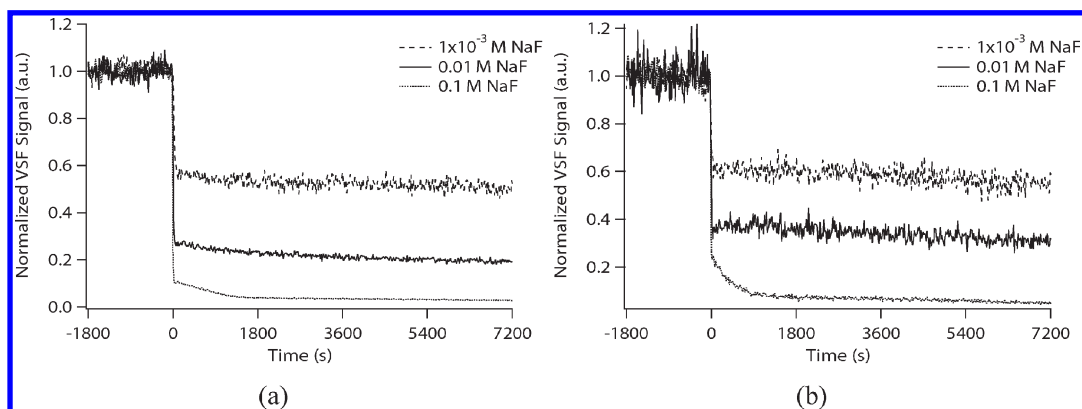


Figure 4. VSF signal at (a) 3200 cm^{-1} and (b) 3600 cm^{-1} monitored over time for three concentrations of NaF: 1×10^{-3} , 0.01, and 0.1 M at the CaF_2 /water interface. The data are all normalized to 1, and time = 0 corresponds to the beginning of signal decay.

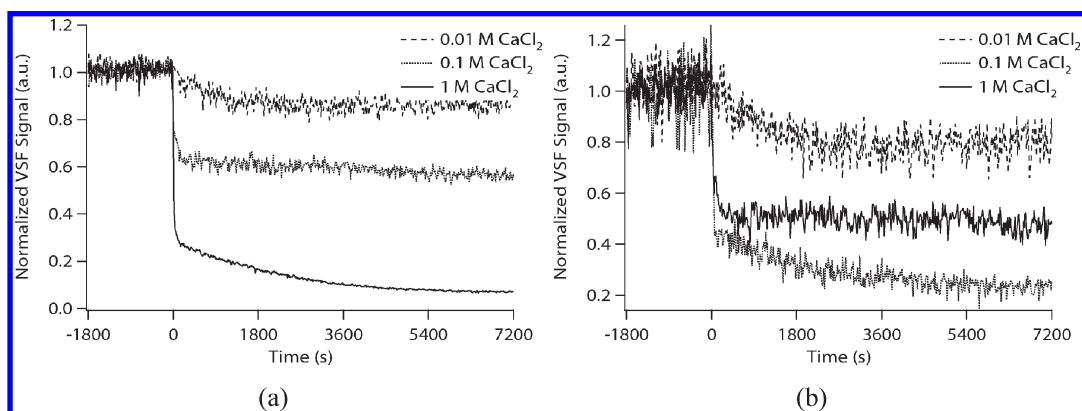


Figure 5. VSF signal at 3200 cm^{-1} (a) and 3590 cm^{-1} (b) monitored over time for three concentrations of CaCl_2 : 0.01, 0.1, and 1 M at CaF_2 /water interface. The data are all normalized to 1, and time = 0 corresponds to the beginning of signal decay.

interfaces^{21,22} and attributed it to surface restructuring. However, those results were observed over a longer time scale, not the intermediate time scale phenomenon of an hour seen here. Our studies over a longer time scale show small changes in the VSFS spectra, but they are difficult to decouple from instrumental drift.

Drawing from the results of the spectroscopic studies discussed above that attribute the spectral features near 3200 cm^{-1} and 3590 cm^{-1} respectively to water directly hydrating the CaF_2 surface with excess F^- and water solvating F^- ions in the interfacial region, we attribute changes in this intermediate time regime to direct interactions between F^- and the CaF_2 surface. Unlike the other anions, F^- is a constituent of the solid CaF_2 . It has long been known that the CaF_2 surface is fluoride deficient in contact with water. Exposing such surfaces to solutions containing more than the equilibrium concentration of aqueous F^- will naturally shift the chemical equilibrium at the interface and thus affect surface speciation. Note that very strongly hydrated F^- can immediately screen surface charges when adjacent to the surface, but for direct bonding to CaF_2 sites at the surface at least part of the hydration shell must be removed. Removing this solvation shell and displacing the surface hydration layer will slow down reactions between F^- ions and the surface, which rely on direct F^- contact.

To test these ideas further, the same experiments at 3200 and 3590 cm^{-1} were performed with CaCl_2 at 0.01, 0.1, and 1 M ionic strengths at pH 5.8 as shown in Figure 5. Calcium has been previously shown to be a potential determining ion for flat CaF_2 surfaces,²² meaning that it can directly interact with the surface, but to have no significant effect on the zeta-potential of powdered CaF_2 below 0.01 M.³³ The kinetic traces bear this out, with no significant change in the VSF signal the ionic strength is greater

than 0.01 M. Given the strongly hydrated nature of CaF_2 ,^{21,34} it might be expected that there would be a significant time lag between the introduction of Ca^{2+} ions to the interface and equilibrium due to the ions having to displace the surface bound water molecules. This is evidenced by the CaCl_2 kinetic traces at both wavelengths. The kinetic traces show two distinct signal decay processes: a rapid decrease and an intermediate time scale decay. The intermediate time scale component is most clearly apparent when the surface is exposed to the 1 M Ca^{2+} solution. The time scale of this feature, around 3600 s, is longer than that seen in the NaF traces. This may be due to the flow rate as solubility studies have shown that small changes in the flow rate and pH in the range from 5 to 7 can have a very large effect on the dissolution rate.⁴⁴ More likely, it is due to the electrostatically unfavorable interaction of Ca^{2+} with the positively charged surface and differences in the hydration of Ca^{2+} and F^- .

Given the similarity of the kinetic results of the F^- and Ca^{2+} , we can conclude that these ions have similar interactions with the interface. These interactions are governed by at least two different time scale processes based on the interfacial structure. The processes are screening and direct surface interaction. The initial rapid decrease in signal is accounted for by the presence of ions in the interfacial region, which screen the surface charge and reduce the thickness of the diffuse layer in a few seconds. The second process, direct interaction, is most clearly seen in the ion kinetics studies at high concentrations which reveal the dynamics of the surface layers. This process is most likely due to the direct interactions of F^- and Ca^{2+} with the CaF_2 surface in which the

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ions chemically adsorb to the surface and displace hydrating water molecules and has a time scale on the order of an hour. It is evident that the decay at 3200 cm^{-1} is related to ion adsorption, as it tracks closely with the decay at 3600 cm^{-1} , which monitors the solvated ion peak. This conclusion seems to run counter to recent electrokinetic studies showing that F^- is not a potential determining ion, in which the strong hydration of CaF_2 and F^- has been used to explain the inability of F^- to reverse the zeta-potential.^{21,22} However, our studies do not find an orientation reversal of the coordinated interfacial water molecules, which would be expected if F^- adsorption reversed the surface charge. Rather, we have evidence for direct adsorption on the surface as seen by the strong presence solvated F^- at 3617 cm^{-1} , a peak that we attribute to water hydrogen bonded to surface bound F^- at 3225 cm^{-1} and a time scale component in the adsorption process similar to that of an ion, Ca^{2+} , known to affect the zeta potential of the surface and alter the chemical equilibrium.

Conclusions

We have performed VSFS experiments in the frequency and time domains to examine the behavior of aqueous Cl^- , Br^- , F^- , and SO_4^{2-} at the $\text{CaF}_2/\text{H}_2\text{O}$ interface. These experiments have been performed under constant flow conditions to allow rapid changes of solution and to prevent a buildup of surface dissolution products, which have affected previous VSF studies in this spectral region. The primary effect of the addition of Cl^- and Br^- ions is to screen the electrostatic field existing at the $\text{CaF}_2/\text{water}$ interface due to its positively charged surface. Aqueous Cl^- and Br^- slightly alter the water bonding structure with Br^- appearing to have the larger effect. We attribute this to the greater polarizability of

Br^- relative to Cl^- . The strongly hydrated SO_4^{2-} ion has a more disruptive effect on the interfacial water–water hydrogen-bonding network; solvated SO_4^{2-} ions are clearly present near the surface. Because of its greater charge, SO_4^{2-} is more effective at screening the surface charge and more strongly attracted to the interface than Cl^- or Br^- . However, our kinetic studies show that the effects of SO_4^{2-} , as well as Cl^- and Br^- , on interfacial water are primarily electrostatic in nature. The kinetic studies show a clear difference in the surface interaction of F^- relative to the other ions. The addition of F^- to the system results in both the rapid electrostatic effect of compressing the double layer as seen in Cl^- , Br^- , and SO_4^{2-} and a slower direct interaction with the mineral surface. Fluoride significantly disturbs the interface as its strong ion–water interactions disrupt the interfacial H_2O – H_2O and H_2O – CaF_2 interactions. The presence of added F^- shifts the solubility equilibrium of the surface, resulting in F^- ions possibly adding to sites on the CaF_2 lattice, shedding their own hydration shells and partially displacing the surface hydration layer. The direct interaction of F^- ions with the surface is supported by the VSF spectrum of interfacial water.

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Supporting Information Available: Equilibrium CaCl_2 salt series spectra and VSF kinetic traces at 3590 cm^{-1} of NaCl , NaBr , and Na_2SO_4 . This material is available free of charge via the Internet at <http://pubs.acs.org>.