# Surface Speciation at Solid/Liquid Interfaces: A Vibrational Sum-Frequency Study of Acetate Adsorption at the Fluorite/Water Interface

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Vibrational sum-frequency spectroscopy (VSFS) has been used to investigate the adsorption of acetate at the fluorite/water interface in situ. The bulk pH value was varied to control the composition of the liquid phase in contact with a single crystalline fluorite ($CaF_2$) surface. Spectra were recorded in frequency regions corresponding to vibrational modes of the adsorbate and water. Quantitative information on interfacial water molecules in different states of order was obtained from the present data. Furthermore, the effect of background electrolyte concentration was studied, and it was found that surface hydroxyls play a crucial role for the oriented adsorption of acetate ions at the interface.

## 1. Introduction

Adsorption phenomena at charged interfaces are of great importance for a variety of processes in nature and industry and have therefore been studied for a long time. However, many powerful methods of surface science only work under ultrahigh vacuum (UHV) conditions, which do not resemble the aqueous environments usually encountered. This is especially true for the solid/aqueous boundary, which is ubiquitous, but, as a buried interface, is not easily accessible experimentally. In favorable cases, specialized techniques, like surface-enhanced infrared (IR) spectroscopy, can be used to investigate the adsorbate, but information on the surface states of water is even more difficult to obtain due to its usually large and overwhelming bulk response. Furthermore, most studies were so far limited to substrates with a high specific surface area, such as finely divided powders or nanoparticle layers. Such materials show a high concentration of surface defects making the interpretation of the results in terms of an intact crystalline surface difficult. For a single crystalline surface, the fraction of surface molecules probed within the detection range of linear IR techniques (on the order of micrometers) is generally not large enough to allow for a separation of the interfacial from the bulk response. For this work the inherent properties of vibrational sum-frequency spectroscopy (VSFS) can be exploited to gain insights into the interface structure at a molecular level. VSFS is based on a nonlinear optical process, which only gives rise to a signal in a system with broken inversion symmetry, e.g., at interfaces. Additionally, a beam geometry close to total internal reflection can be used to dramatically enhance the sensitivity.[1]

In recent years, a number of adsorbates have been studied at the solid/liquid interface,[2] mostly surface-active compounds (surfactants) including long-chain carboxylates. All these studies were performed at near-neutral pH and revealed the importance of surface charge for the adsorption process, but to our knowledge, experimental work by VSFS on adsorption processes at different pH values remains limited. For some neat solid/water interfaces, e.g., with quartz,[3] sapphire,[4] or fluorite ($CaF_2$)[5] as the solid phase, the effect of pH has been studied previously and dramatic variations of water structure were found. Briefly, the relative concentrations of surface species, which can carry positive, negative, or no charge, change with pH. At a given pH, either positively or negatively charged sites will dominate and surface charging occurs (positive for lower, negative for higher pH), which generates a strong electric field (ranging up to $10^7$ V·cm$^{-1}$ [4]) at the interface. Except at the isoelectric point (IEP) of the surface, i.e., when positively and negatively charged ions are exactly balanced, water molecules near the surface orient along the field and give rise to a nonzero second-order surface susceptibility, observable by VSFS. Based on these microscopic phenomena at the interface, the spectral response of hydrogen-bonded water molecules is characterized by two broad resonance features, located at ∼3200 and ∼3450 cm$^{-1}$.[3−7] The latter has similarities to hydrogen-bonded stretching modes in bulk liquid water and is usually assigned to a collection of water molecules in a rather disordered state.[8] The 3200 cm$^{-1}$ band is commonly attributed to a collection of water molecules within a more symmetric bonding environment, commonly referred to as a tetrahedral hydrogen bond network. It was also shown that the net total water VSF amplitude strongly depends on the extent of surface charging.[4,5] This sensitivity of VSFS for interfacial water enables us to investigate the screening effect of surface charge by anionic adsorbates (e.g., carboxylates) on water structure, and at the same time, the adsorption process can be followed by monitoring the VSFS signatures of the head group and the hydrocarbon moiety (alkyl chain).[9]

On the basis of electrostatics, anion adsorption generally only takes place at positively charged surface sites. The VSF spectra then contain information on the structure of the adsorbate, and frequency shifts can be exploited to characterize substrate−adsorbate interactions. Of particular interest are also effects of the strong electrical field at the interface on the dissociation equilibria, kinetic aspects of the adsorption process, and the competition between different ions at the interface. Furthermore, the role of fluorite surface species in the adsorption process and their effect on the orientational distribution of adsorbates close to the interface poses interesting questions where VSFS can provide insights.

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## 2. Background

VSFS is a second order nonlinear optical process, and its theory has been extensively discussed.[8,10] In essence, sum-frequency generation is forbidden in bulk centrosymmetric media, but at interfaces symmetry reduction results in an effective surface nonlinear susceptibility $\chi^{(2)}_{\mathrm{eff}}$, which arises from the net orientation of molecular hyperpolarizability contributions toward the interface. Accordingly, sum frequency generation, which is a coherent process, is allowed at the interface and the various elements of $\chi^{(2)}_{\mathrm{eff}}$ can be probed by selecting suitable combinations of beam polarizations. For this study, all spectra were obtained using the ssp polarization scheme. These three polarization indices represent light polarized parallel to the plane of incidence (p) or perpendicular to the plane of incidence (s), and their order is in decreasing frequency. In this case, sum-frequency and visible probe beams are s polarized, whereas the tunable IR beam is p polarized.

## 3. Experimental Details

Details of the laser system[9] and experimental setup[5] have been reported. For the current VSF experiments, the IR and visible (532 nm) laser pulses (duration ~30 ps, produced by a commercial laser and parametric oscillator/amplifier) were incident on a $CaF_2$ prism (68°) at near critical angle, 17° and 20.5°, respectively. Spacial and temporal overlap at the interface was established, and the resulting sum-frequency photons were selected by narrow-band filters and converted into electric signals by a photomultiplier attached to a monochromator. The design of the prism cell was modified to facilitate changing of the bulk composition. This was achieved by covering the top of the prism with a cylindrical part made from KelF (polychlorotrifluoroethylene), connected to PTFE tubing. A peristaltic pump was then used to constantly flush the prism surface with sample liquid. This is especially important for weakly buffered solutions to avoid any changes of the pH during measurements. The pH of the pump's reservoir was continuously monitored during the experiment by a calibrated pH meter connected to a glass electrode. For some of the samples, the VSFS response was monitored for several hours to ensure full equilibrium of the interface.

Solutions of varying pH were prepared by mixing two stock solutions containing either 45 mM acetic acid, 45 mM sodium chloride and 5 mM hydrochloric acid, or 45 mM sodium acetate and 50 mM sodium chloride. At such low concentrations, volume effects of mixing can be neglected, and the chloride concentration of the resulting mixtures is constant (50 mM). The solutions of highest pH (9.2−9.3) contained trace amounts of sodium hydroxide. Although experiments without added sodium chloride showed only a small change of the spectra, keeping the anion concentration constant (except for the adsorbate, i.e., acetate) is essential for this type of study to avoid complications from any major variations of the ionic strength of the solution, which may affect chemical equilibria and the structure of the interface.

Reagents of analytical purity and high purity water obtained from a Barnstead NANOpure II system (resistivity >18 MΩ·cm) were used throughout. All glassware was cleaned by prolonged soaking in concentrated sulfuric acid with added ammonium peroxodisulfate and rinsing with copious amounts of purified water. The surface of the $CaF_2$ prism was regularly polished with 0.05 $\mu$m $Al_2O_3$ powder.

## 4. Results and Discussion

Acetate adsorption has been investigated recently[9] and was chosen for this study because its p$K_a$ value (4.76[11]) is close to numerous other organic acids which are commonly found at solid/liquid interfaces. Experiments showed that the adsorption process is rapid and fully reversible. Furthermore, it does not render the fluorite surface strongly hydrophobic (as would be the case for long-chain carboxylates, which tend to precipitate at low pH values because of the vanishing solubility of the free acids and their calcium salts). Details of the VSF spectra of adsorbed acetate have been discussed elsewhere.[9] In short, the spectral response is characterized by a broad band at ~1455 cm$^{-1}$. It is composed of two modes, a low-frequency vibration (at ~1450 cm$^{-1}$) arising from a combination of $\nu$CO, $\nu$CC, and deformation modes ($\delta$OCO, $\delta CH_3$), and a more localized $\delta CH_3$ deformation mode at ~1464 cm$^{-1}$.[9] For simplicity, these contributions will be referred to as the (a) and (b) mode. Additionally, a $CH_3$ symmetric stretch resonance is found at ~2950 cm$^{-1}$.

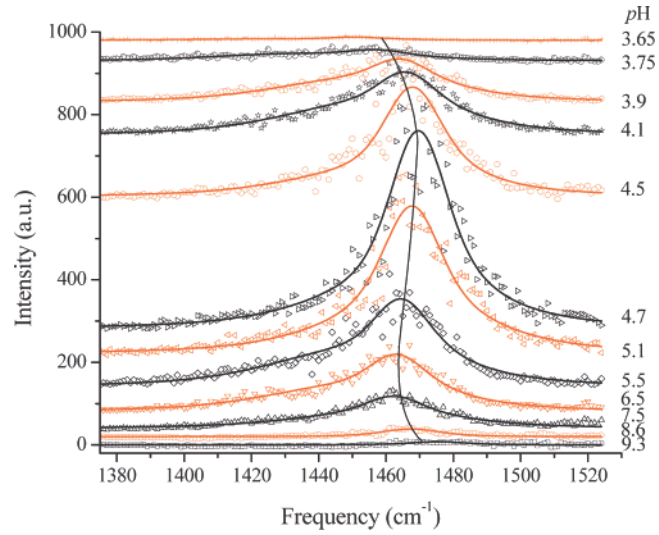


**Figure 1.** VSF spectra (ssp) of the sodium acetate (aq)/$CaF_2$ interface in the 1375 to 1525 cm$^{-1}$ frequency region as a function of pH (from top to bottom): 3.65, 3.75, 3.90, 4.10, 4.50, 4.70, 5.10, 5.50, 6.50, 7.47, 8.60, and 9.29. Curve fits shown as solid lines. Some of the data and fits were omitted for clarity.

The present VSF spectra of acetate adsorbed onto the fluorite/water interface as a function of bulk pH are shown in Figures 1 (1375−1525 cm$^{-1}$) and 2 (2800−3800 cm$^{-1}$). No additional peaks of significant intensity could be detected using any of the unique polarization combinations within a frequency range from 1250 to 4000 cm$^{-1}$, in agreement with our previous findings.[9]

To quantify the results, the spectra were decomposed into a nonresonant background and $i$ individual modes.[2] A coherent superposition of resonances arising from effective nonlinear susceptibilities $\chi^{(2)}_{\mathrm{eff},i}$ was used, with the individual contributions represented by eq 1:

$$\chi^{(2)}_{\mathrm{eff},i} = A_i\, \mathrm{e}^{\mathrm{i}\gamma_i} \int_0^\infty \frac{1}{\omega_{\mathrm{IR}} - \omega_{\mathrm{L}} + \mathrm{i}\Gamma_{\mathrm{L}}} \exp\left[-\frac{(\omega_{\mathrm{L}} - \omega_i)^2}{\Gamma_i^2}\right] \mathrm{d}\omega_{\mathrm{L}} \quad (1)$$

where $A_i$, $\gamma_i$, $\omega_i$, and $\Gamma_{\mathrm{L}}$ are the amplitude, phase, center frequency, and homogeneous (Lorentzian) linewidth of the $i$th mode. Inhomogeneous broadening was accounted for by a Gaussian distribution of width $\Gamma_i$. Given the spectral width of the IR beam (~6 cm$^{-1}$) and thus $\Gamma_i \gg \Gamma_{\mathrm{L}}$, the peak shape is not sensitive to $\Gamma_{\mathrm{L}}$ and a constant value $\Gamma_{\mathrm{L}} = 5$ cm$^{-1}$ was used throughout. The values of $\Gamma_i$ did not vary significantly for the pH range studied and were thus determined from global fits of

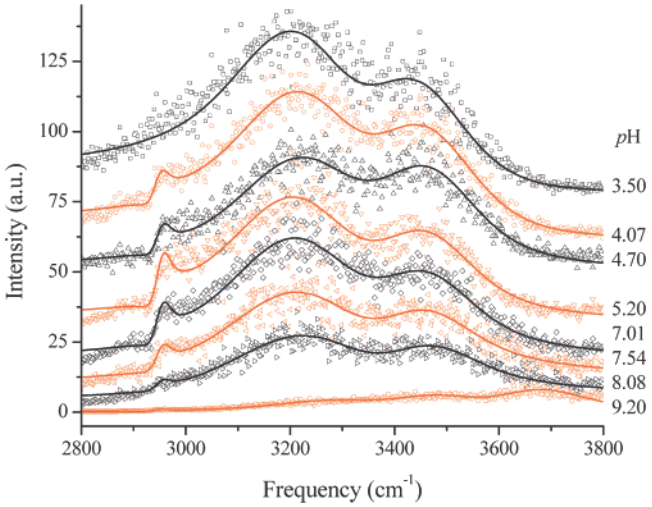


**Figure 2.** VSF spectra (ssp) of the sodium acetate (aq)/$CaF_2$ interface in the 2800 to 3800 cm$^{-1}$ frequency region as a function of pH (from top to bottom): 3.50, 4.07, 4.70, 5.20, 7.01, 7.54, 8.08, and 9.20. Curve fits shown as solid lines. Some of the data and fits were omitted for clarity.

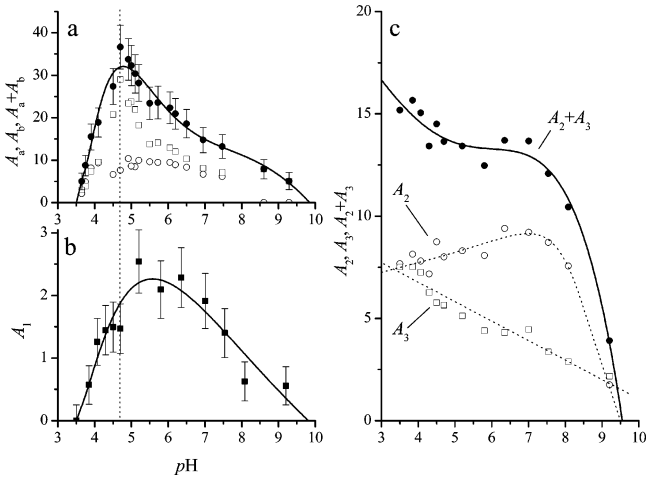


**Figure 3.** Amplitude of the acetate bands $A_a/A_b$ (○, $A_a$; □, $A_b$) (a) and the symmetric $CH_3$ stretch, $A_1$ (b). Amplitudes of the two water bands observed at 3250 cm$^{-1}$ (○, $A_2$) and 3425 cm$^{-1}$ (□, $A_3$) are also shown. Solid lines are guides for the eye only.

a subset of the spectra. The same applies to the peak position of $\nu CH_3$ which was fixed at 2950 cm$^{-1}$, except for the lowest and highest pH values.

**4.1. Spectral Contributions of the Adsorbate.** Figure 3a,b shows the adsorbate-related amplitudes obtained from our analysis of the spectra. For both spectral regions, a maximum for acetate adsorption is found at pH ≈ 5, somewhat higher than the p$K_a$ of acetic acid (4.76 at 25 °C[11]).

This indicates that there are two counteracting effects which determine the amount of acetate adsorbed at the surface: the surface charge density and the bulk acetate concentration, which are both strongly pH dependent. The latter can be easily obtained from the equilibrium constant of acetic acid dissociation (p$K_a$ = 4.76 at 25 °C[11]) and the (known) pH (Figure 4a). An analysis of the charge density at the fluorite interface is more difficult to carry out, as it cannot be measured directly. Wu et al.[12] performed a comprehensive potentiometric study and successfully determined the concentrations of different surface sites present on $CaF_2$(aq) from a thermodynamic equilibrium model. The surface sites are generally composed of two calcium centers with attached hydroxyl or fluoride groups, stabilized by

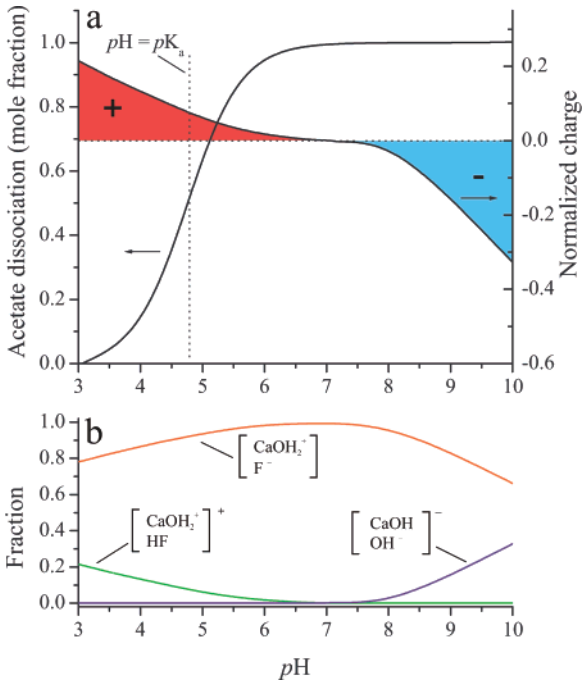


**Figure 4.** (a) Mole fraction of (dissociated) acetate and normalized charge of the fluorite surface as a function of pH. (b) Idealized surface speciation based on the study of Wu et al.[12]

hydrogen-bonding. Their results are shown in Figure 4b, together with the calculated normalized charge density (Figure 4a). Below pH ≈ 7, the concentration of sites with a net positive charge increases because of fluoride protonation at the interface; at higher pH, fluoride ions are exchanged by hydroxyl ions, thus leading to an increase in the population of net negatively charged sites. It should be noted that the actual surface charge of fluorite might be slightly more positive than predicted by the model of Wu et al.,[12] as it does not consider isolated $\equiv CaOH_2^+$ species generated by preferential solvation of $F^-$ lattice ions[13] in the vicinity of a calcium surface site.

Care has to be taken not to confuse the surface charge with the potential in the plane of hydrodynamic shear, the so-called zeta potential, which can be conveniently obtained from electrokinetic experiments.[13,14] By definition, at pH = IEP, the zeta potential equals zero. For $CaF_2$, a broad IEP range has been reported, ranging from 6.2 to 10.6.[15] In systems containing a non-negligible concentration of ions, the position of the isoelectric point depends on the distribution of ions near the surface, which is governed not just by electrostatics but also by steric effects, ion−ion correlations, and specific interactions. Thus, the IEP can significantly differ from the point of charge neutrality directly at the surface. In fact, positive zeta potentials were reported up to pH ≈ 10.[13,14] It has also been shown that surface carbonation,[13,14] which commonly occurs on fluorite in alkaline medium, can significantly affect the zeta potential.[14,15]

In the current case, the effect of pH on the fluorite/acetate interaction can be divided into three regions:

**pH ≳ 8.** With increasing bulk pH, the concentration of positively charged surface sites is rapidly diminished. Some adsorption can still take place at $OH_2^+/F^-$ sites. With the presence of $OH/OH^-$ species at even higher pH, acetate adsorption is rendered electrostatically unfavorable by the net negative charge of the surface.

**5 ≲ pH ≲ 8.** Although the bulk acetate concentration is virtually constant, adsorption is governed by the net surface

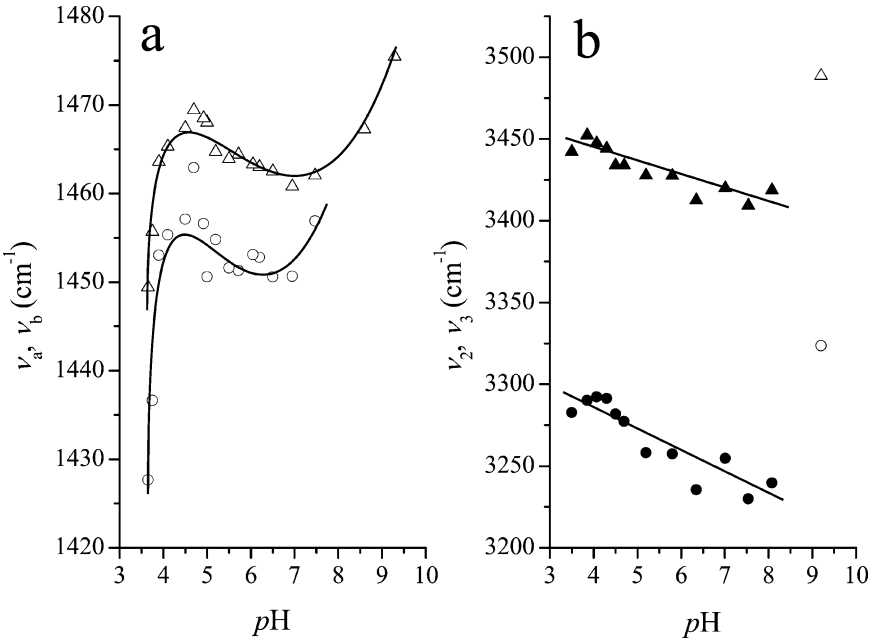


**Figure 5.** Positions of the acetate bands $\nu_a/\nu_b$ (○, $\nu_a$; △, $\nu_b$) (a) and the water bands $\nu_2/\nu_3$; open symbols are data at pH 9.3, see text) (b). Solid lines are guides for the eye only.

charge of the substrate. The surface charge is increasingly positive toward lower pH because of the formation of $OH_2^+$/HF sites.

***p*H ≲ 5.** Protonation of acetate ions leads to a rapid decrease of available acetate ions around pH ≈ p$K_a$. Thus, the acetate adsorption equilibrium is shifted toward lower surface coverage.

Concerning this rapid decline of adsorption at low *p*H, the similar trend for the a/b modes ($A_a$, $A_b$; Figure 3a) and the $\nu CH_3$ symmetric stretch ($A_1$; Figure 3b) indicate that undissociated acetic acid (HAc) is not adsorbed at the interface within the sensitivity of VSFS, because the $\nu CH_3$ mode, apart from a small shift in energy, should be retained for HAc. Additional experiments were performed with a diluted (10%) HAc (aq) solution not containing any electrolytes. No peaks were found either in the $\nu$C═O or $\nu CH_3$ region of the VSF spectrum. This further corroborates the sole presence of dissociated acetate at the interface. The individual contributions of the a and b mode to the total VSF amplitude in the 1375−1525 cm$^{-1}$ spectral region, Figure 3a, show some differences in their trends, but we refrain from an analysis of the individual amplitudes due to the overlap and broadening of both bands which renders them inseparable at high amplitudes.

**4.2. Water Response.** In addition to the adsorbate contributions, the VSF spectra also contain information on interfacial water species. The two bands commonly found at the neat $CaF_2$/water interface[5] and already mentioned above were also found in the current spectra (Figure 2). The amplitudes $A_2$ and $A_3$ (Figure 3c), related to the bands at ∼3250 and ∼3425 cm$^{-1}$, show a rapid increase at pH ≈ 8.5 (surface charge neutrality), which arises from the orientation of water molecules at the surface which becomes increasingly positively charged toward lower pH.

Interestingly, the amplitude $A_2$ attributed to more well-ordered, tetrahedrally bonded $H_2O$ molecules reaches a plateau value at near neutral pH (Figure 3c), whereas $A_3$, associated with the VSF response of more disordered water, almost linearly increases when the pH is lowered, following the trend of the (increasingly positive) surface charge. The total water amplitude first seems to level off around pH ≈ 7 but further increases at low pH. Notably, the start of this increase coincides with the declining acetate adsorption at pH ≈ p$K_a$ caused by the rapid decrease of the bulk acetate concentration. This enables a larger number of positively charged surface sites to interact with water. The chloride ions present as background electrolyte are apparently not forming a layer dense enough at the interface to fully compensate these charges immediately at the interface. Moreover, the orienting interfacial field extends considerably into a diffuse ion layer close to the solid/liquid boundary, allowing a considerable volume of water near the interface to contribute to the sum-frequency response.

The much weaker substrate−adsorbate interaction at low pH (pH ≲ p$K_a$) is also evidenced by the significant decrease in band energy (Figure 5a), which most likely arises from the protonation of acetate leading to a single-bond character of the carboxylate C−O bond. At higher pH, the peak frequency is rather insensitive to bulk pH up to the point of charge neutrality at the surface (pH ≈ 8.5), only slightly decreasing by ∼5 cm$^{-1}$. This indicates a relatively constant molecular environment for the adsorbed acetate ion and only small coverage-dependent effects, which could either be caused by adsorbate−adsorbate interactions or depolarization of the interface by other ions within the intermediate pH range. The substantial amounts of interfacial water present up to high acetate concentrations found in our previous study[9] would also be at odds with the formation of the dense acetate layer prerequisite for any intermolecular interactions.

The bands associated with hydrogen-bonding water modes also show upward shifts toward lower pH ($\nu_2$, $\nu_3$; Figure 5b). With an increasing (positive) charge density at the interface, the strength of the overall hydrogen bonding seems to increase slightly, which was deduced from the effect of pH on the $A_2 + A_3$ amplitudes. This is due to several factors related to the higher surface field including more contribution from water molecules in the double layer that reside deeper into the solution with strong bonding and enhanced structuring. At the highest pH studied (9.3), the spectrum from 2800 to 3800 cm$^{-1}$ significantly differs from the spectra at lower pH: an additional band at 3650

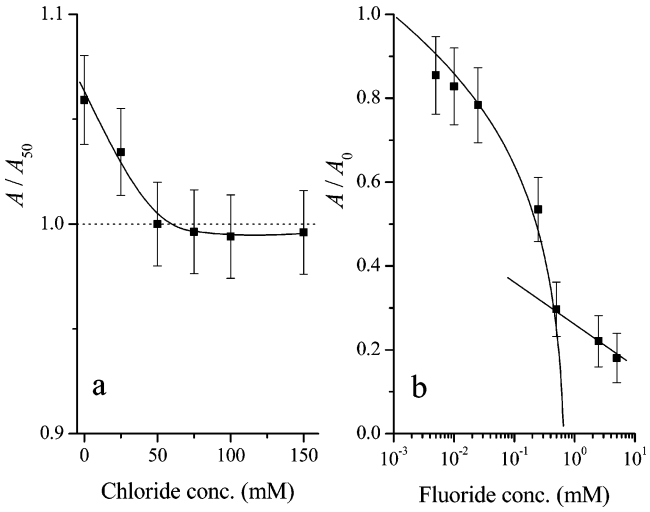


**Figure 6.** (a) VSF amplitude $A = A_a + A_b$ as a function of bulk chloride concentration (in mM), normalized by the amplitude at 50 mM sodium chloride (aq), $A_{50}$. (b) Normalized amplitude $A/A_0$ as a function of fluoride concentration (in $\mu$M). $A_0$ corresponds to the sample without added fluoride. Curves show trends only.

$cm^{-1}$ appears and was attributed to weakly bonded Ca−OH oscillators at the solid/liquid interface in an earlier report.[5]

**4.3. Role of Specific Interactions.** To further elucidate the driving force of surface-acetate adsorption and the role of surface charge screening by the background electrolyte, additional experiments were performed. The chloride content of the mixtures was varied while keeping the acetate concentration constant at 45 mM (pH = 6). Figure 6a shows the normalized amplitude of the a/b modes. Interestingly, even at high background electrolyte concentration, $c(\mathrm{NaCl}) \gg c(\mathrm{NaAc})$, acetate adsorption dominates and chloride ions only very moderately interfere. At a first glance, this may appear surprising because chloride and acetate are both monovalent ions and only weakly hydrated in water. Thus, the stability of the carboxylate−surface interaction cannot be solely explained by electrostatics; there must be an additional free energy effect as well. At high chloride concentrations, chloride ions would otherwise be the predominant ions screening the (positively charged) surface. It can also be inferred from the data presented in Figure 6a that acetate adsorption happens directly at the surface rather than by electrostatic interactions in the double layer.

At the water/$CaF_2$ interface, acetate/fluorite interactions will take place via the specific surface sites discussed above (Figure 4). Only the $\equiv$Ca−$OH_2^+$ species carries a positive charge and thus seems to be the most likely group to interact with acetate ions. Naturally, this (positively charged) entity will electrostatically interact with all anions (acetate, chloride) present in the aqueous phase, but the stability of the surface complex will largely depend on the basicity of the anion. Thus, the reason for the different affinity of acetate and chloride, respectively, toward the $\equiv$Ca−$OH_2^+$ sites despite their equal charge can be found in the much larger basicity of acetate. Higher basicity is favorable for the formation of more stable surface complexes of the type $\equiv$Ca−$OH_2^+$···$A^-$ (A = acetate). By analogy, acetic acid is less dissociated in water than hydrochloric acid.

The chemistry of the fluorite surface also explains the release of acetate at low pH already discussed. Upon protonation, the interaction $\equiv$Ca−$OH_2^+$···AH is no longer favorable enough to cause significant adsorption and acetic acid is released from the surface.

To further corroborate the assumption that the stability of the substrate−adsorbate surface complex is mainly controlled by the basicity of the adsorbate and not by any specific oxygen−calcium interactions or other effects, the very weakly basic trifluoroacetate ion ($pK_a = 0.52$[11]) was checked for its adsorption tendency (at concentrations of 45 mM and 333 mM; pH $\approx$ 6; no added NaCl). It features the same carboxylate headgroup and a strong dipole moment, but $CF_3$ is substituted for $CH_3$ in acetate. No signals could be detected in either the carboxylate or the $\nu$CF region of the VSF spectrum, while control measurements with sodium acetate under identical conditions revealed strong sum-frequency signals related to acetate adsorption.

This finding supports the proposed adsorption mechanism for acetate by formation of an acid−base complex, i.e., an ion pair attached to the surface. The adsorption is reversible and a dynamic equilibrium between bulk and adsorbed acetate is rapidly established when a solution containing the adsorbate is brought in contact with the fluorite surface. Acetate ions are continuously exchanged between the bulk and the adsorbate layer. The average lifetime of the acetate−substrate complex cannot be easily estimated, but it is certainly longer than common lifetimes of similar ion associates found in solution (on the order of nanoseconds[16]). The upper limit is given by the experimentally observed immediate disappearance of all acetate bands when the prism is flushed with water (estimated time frame 100 ms to 1 s).

Especially in solutions without added chloride, acetate molecules are not only adsorbed directly at the surface but also act as a background electrolyte screening the surface charge as part of the double and diffuse ion layers. Keeping in mind that VSFS specifically probes all molecular hyperpolarizability contributions with a net orientation toward the interface, a sum-frequency response will be measured not only for adsorbates directly bonded to the substrate. For example, for water molecules, such a net orientation can extend several molecular layers into the liquid phase by the action of the double layer at the interface. Water molecules, however, show a high degree of intermolecular orientational correlation via the H-bond network. Such correlations may amplify relatively small molecular orientational forces into an appreciable net orientation of an associated network. From previous VSFS studies, it is not clear if net orientation is also observable for rather isolated small dipolar molecules in the ion layers near a charged surface (acetate, trifluoroacetate) or if direct interaction with surface sites is prerequisite for such molecules to generate sum-frequency signals.

This question can be readily answered from the experiments at the sodium trifluoroacetate(aq)/$CaF_2$ interface. For bulk solutions not containing any other anions than acetate or trifluoroacetate, a similar structure of the ionic double layer and diffuse layer at the interface can be inferred. Thus, the number density of adsorbate molecules near the interface should be comparable. However, only for acetate could a notable sum-frequency response be measured and it is thus evident that electrostatic interaction alone is not enough to give rise to any major overall orientation of the adsorbate anions toward the surface, even at high concentration. Otherwise, bands of comparable intensity should show up in the trifluoroacetate spectra. Screening of surface charges is apparently established by trifluoroacetate (or partly by acetate) counterions, which are randomly oriented despite their dipole moment and therefore not detectable by VSFS. Only for ions of sufficient basicity (like acetate) are longer-lived complexes showing a net orientation of the acetate molecular hyperpolarizability toward the interface formed directly at the surface, and these are the only species that show up in the VSFS spectra. Additional orientation-

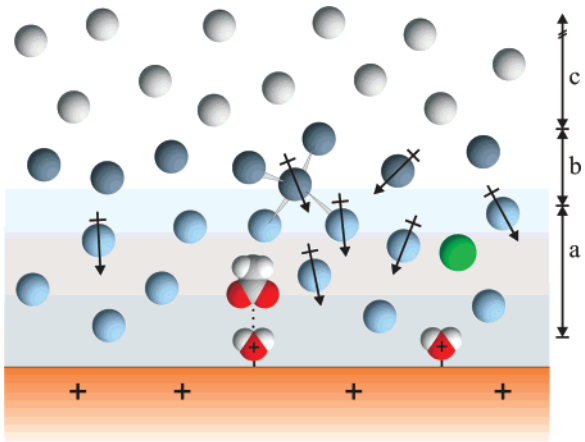


**Figure 7.** Expanded view of the interface region. Water species are represented by blue (regions a and b; see text) and gray spheres (region c; molecules with no net orientation). Acetate and chloride (green) ions are also shown. Arrows indicate the unit vector of the $H_2O$ dipole moment.

stabilizing effects by adsorbate−adsorbate interactions (formation of stable monolayer or bilayer structures, etc.) are also not present for (trifluoro)acetate anions.

**4.4. Substitution of Surface Sites.** It has just been noted that only direct surface−substrate interactions lead to an oriented adsorption of acetate at the fluorite/water interface. Furthermore, surface species of the type $\equiv CaOH_2^+$ seem to be the most likely interaction partners for adsorbed acetate. Within this picture, only negligible orientational bonding of the carboxylate should take place at a $CaF_2$ surface lacking −OH functionalities. Fortunately, such a modification can be achieved experimentally with relative ease by adding small amounts of fluoride to the bulk medium, at least for pH $\lesssim 8$.[12] Within this pH range, the solubility products of $Ca(OH)_2$ and $CaF_2$, which may act as an indication for the prevalent surface species, differ by several orders of magnitude, $K_{SP}(Ca(OH)_2) \gg K_{SP}(CaF_2)$ ($5.02 \times 10^{-6}$ and $3.45 \times 10^{-11}$,[11] respectively). Consequently, the equilibrium concentration of $F^-$ for a saturated fluorite solution is only ~0.3 mM and even low concentrations of soluble fluoride (added as NaF) appreciably suppress hydroxyl formation at the solid/liquid interface. Experimental data are presented in Figure 6b, which clearly shows that concentrations in the micromolar range are already effective. At concentrations of NaF as low as 1 mM, fluoride is substituted for a large fraction of the surface hydroxyls and the carboxylate bands indicating oriented acetate adsorption in the VSF spectrum reaches a low plateau value. Note that at millimolar fluoride concentrations the bands are extremely broadened and close to the noise level of the nonresonant background, which was considered constant for all samples. The remaining amplitude at NaF concentration >1 mM may also be partly caused by residual surface hydroxyls as a complete substitution of all interacting $\equiv CaOH_2^+$ species by fluoride seems to be unlikely. Interestingly, the overall electrostatic structure of the interface (as measured by the zeta potential) is surprisingly insensitive to the bulk fluoride ion activity up to at least 10 mM[13] and thus cannot be held responsible for the dramatic changes in acetate adsorption, in agreement with our findings for the trifluoroacetate ion, which pointed out the importance of stabilized surface−adsorbate species to the establishment of oriented adsorption of dipolar molecules at the interface.

**4.5. Overall Picture.** A schematic view of our interpretation of the acetate(aq)/fluoride interface at an intermediate pH is given in Figure 7. Two different species of water exist at the interface, partly tetrahedrally coordinated (dark blue) molecules further away from the interface and more disordered molecules closer to the surface (light blue). The amplitude of the latter ($A_3$, Figure 3c) increases markedly with decreasing pH due to a higher degree of structuring caused by a stronger electrical field at the interface. The positive charge of the surface leads to the adsorption of acetate at $\equiv CaOH_2^+$ sites, but full surface coverage is not reached at moderate acetate concentrations. Acetate−acetate interactions are weak, and there are no other driving forces that could lead to higher coverage or even charge reversal at the interface. However, the presence of adsorbed ions and of acetate, together with chloride ions, in the diffuse ion layer close to the surface, prevents water molecules from forming a more ordered structure, and many of these water molecules are located within or near the hydration sphere of charge-compensating anions (either chloride or unbound acetate ions). The water molecules interspersed in the ion layers close to the interface act as probes for the electrical field at the interface. As the ion layer balancing the surface charge becomes more diffuse further from the interface, the number of more ordered water molecules increases ($A_2$, Figure 3c; dark blue, Figure 7). In this region, the orienting field appears to be remarkably constant due to the charge-compensating action of the electrical double layer and the adsorbed acetate, and only increases when acetate adsorption becomes unfavorable at low pH.

## 5. Conclusions

The process of acetate adsorption at the aqueous fluorite surface has been investigated in situ by VSFS. We have demonstrated that information about the molecular environment of the adsorbate can be obtained and the effect of surface charge and coverage on peak positions has been studied. In contrast to other methods, the surface specificity of VSFS also allows the direct observation of interfacial water molecules. Two water bands were identified and can be attributed to molecules in different hydrogen-bonding environments. Their amplitudes were correlated with the microscopic environment derived from the adsorption data and explained by the presence of water molecules in different regions of the interface.

Protonated hydroxy surface sites have been shown to play a key role in substrate−carboxylate interactions. Exchange of these sites by fluoride ions leads to a notable decline in acetate adsorption. It has also been demonstrated that the basicity of the adsorbate determines the stability of a short-lived surface complex, which is formed in a fully reversible reaction.

Using VSFS we can show that oriented adsorption of small ions requires the presence of reasonably long-lived ion pairs (surface salts) at the interface, when additional structure-stabilizing effects (formation of ordered clusters/layers/networks) are absent. Anions not interacting with specific surface functionalities or residing in a diffuse ion layer as background electrolyte are randomly oriented in the interface region. Exploiting the unique advantages of VSFS and using water molecules as molecular probes for the electric field close to the interface, we can show that this occurs despite an orienting surface field and the dipole moment of the adsorbate.

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