In Situ Vibrational Spectroscopic Studies of the CaF$_2$/H$_2$O Interface

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In these first vibrational sum frequency spectroscopy studies of the CaF$_2$/H$_2$O interface conducted under varied aqueous phase composition, large changes in the water structure and surface composition have been found. As the pH of the aqueous phase is adjusted from acidic to basic, dramatic changes in the orientation and hydrogen bonding structure of the water molecules are observed, in addition to the clear presence of surface hydroxide species at high pH. Fundamental studies of the pH-dependent behavior of hydrous fluorite surfaces are essential for understanding the reaction mechanisms involved in calcium mineral flotation systems.

Introduction

The interaction of water molecules with solid surfaces is a significant fundamental issue in surface science.[1] Although much research effort has been devoted to interactions of water with insoluble oxide surfaces,[1,2] relatively few studies have examined slightly soluble ionic salts such as fluorite (CaF$_2$) and their surface interactions within an aqueous environment.[3−7] Fluorite is the primary mineral used in the production of hydrofluoric acid and is used in a variety of other industrially significant processes. It is often associated with other calcium-containing minerals, and the efficient separation of these materials is desirable. Separations are typically carried out via mineral flotation,[8] a process which is highly dependent on the surface chemistry of the minerals involved. Due to the slightly soluble nature of CaF$_2$, as well as other calcium containing minerals, the surface chemistry will be influenced by dissolution of the surface ions from the solid phase through interactions with water molecules within the aqueous phase. In addition, the surface properties of the hydrated fluorite are strongly dependent on the solution pH. This acid/base behavior influences the adsorption of complexing agents and surfactants used for separations in these mineral flotation systems.[8] Fundamental investigations are necessary to understand how the CaF$_2$ surface interacts with water molecules at the solid/solution interface and how solution composition and pH affect these interactions.

In this Letter we provide new information about water structure and hydroxide species present at the CaF$_2$/H$_2$O interface as a function of pH and aqueous ion composition. The studies involve measuring the vibrational spectroscopy of the interfacial molecules using the technique vibrational sum frequency spectroscopy (VSFS). VSFS is an inherently surface specific technique with a spectral response limited to molecules within the interfacial region only.[9] This is the first detailed study of water structure in the interfacial region between an ionic salt and an aqueous phase. The experiments conducted show dramatic changes in the hydrogen-bonding environments of water molecules at the interface as the ionic composition and pH of the aqueous phase is altered.

With VSFS, the vibrational signature of surface molecules is generated by coupling two high-intensity, coherent laser beams spatially and temporally at an interface: one, a tunable IR beam (ω_1), and the other, a fixed frequency visible beam (ω_2). The incident laser beams couple to generate a response at the sum of the two incoming frequencies ($\omega_3 = \omega_1 + \omega_2$).[10] With a scan of the IR frequency across a vibrational resonance, the generated sum frequency signal (ω_3) maps out a vibrational spectrum of the probed interfacial molecules. Within the electric dipole approximation, the sum frequency process is forbidden in a bulk centrosymmetric medium but can show a spectroscopic response from molecules within the interfacial region, where the inversion symmetry of the bulk solution is broken. Molecules probed must be both Raman and IR active in order to generate a sum frequency signal. We examine the affect of hydrogen bonding on the OH vibrational modes of water molecules in this interfacial region. Early Raman and IR studies of bulk water,[11,12] as well as more recent VSFS studies of interfacial water,[13] have shown that the energy of these vibrational modes is strongly affected by the degree of hydrogen bonding; therefore, examination of their peak positions and peak widths can provide information on the molecular environments present in the interfacial region.

Experimental Section

Experiments were conducted using a diode-pumped Nd:YAG laser producing 3.5 ns pulses with a repetition rate of 20 Hz. The fixed 1.064 μm output is split into two beams: one passing through a BBO crystal to generate a fixed frequency 532 nm beam, the

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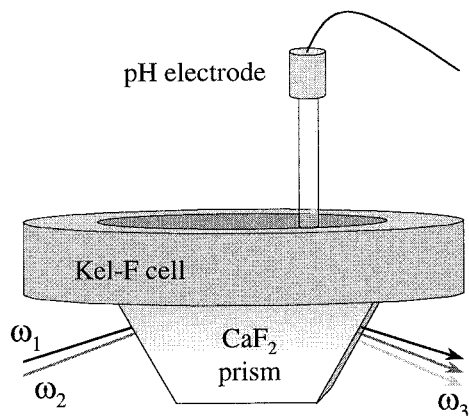(13) Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908−911.

Figure 1. Experimental cell.

other passing through an optical parametric oscillator/optical parametric amplifier (OPO/OPA) system in order to generate an IR beam tunable from 2500 to 4000 cm^{-1} with a bandwidth of ~1 cm^{-1}. Details of the laser system may be found elsewhere.[13] The experimental sample cell consists of a hollow cylinder of Kel-F (polychlorotrifluoroethylene, Boedeker Plastics) placed over the top of a large CaF$_2$ prism (50 × 50 mm) and sealed with an O-ring (Figure 1). The visible and IR beams are directed toward the interface at incident angles at, or slightly above, their respective critical angles. The sum-frequency signal generated from the interface is collected via a PMT detector and gated electronics after passing through filters to remove stray light and the reflected fundamental beams. Data were normalized to fluctuations of the IR power. All spectra were obtained using the following polarization scheme which probes vibrational modes normal to the plane of the interface: sum frequency (s), visible (s), and IR (p). Dilute solutions of HClO$_4$ (70% double distilled) and NaOH (99.998% pure) for pH adjustments were prepared with HPLC grade H$_2$O. The pH of the sample solution was continuously monitored with a glass combination electrode calibrated with pH 4, 7, and 10 standards.

Results and Discussion

In the studies described, the OH stretching bands of water in the 2700–3800 cm^{-1} region have been examined. The VSFS spectra of water molecules in a condensed phase are characterized by energy shifts in the peak responses of the OH stretching modes due to varying degrees of intermolecular hydrogen bonding.[14] Typically, the sharp vibrational resonances found for gas-phase OH stretches at ~3700 cm^{-1} are broadened and shifted to lower frequencies in the condensed phase spectra as water molecules condense and hydrogen bonding between water molecules increases. This is a result of the broad distribution of hydrogen bonding environments experienced by the OH oscillators. Previous VSFS studies[14–16] have characterized these broad spectral features into three main categories: highly ordered water molecules with symmetric, tetrahedral hydrogen bonds whose cooperative vibrational motion gives a broad peak response in the 3100–3200 cm^{-1} range; more disordered asymmetrically bonded water molecules with either asymmetric or bifurcated hydrogen bonds giving a response centered in the 3400–3500 cm^{-1} range; and a sharper peak response from weakly coupled or uncoupled "free-OH" oscillators in the 3600–3700 cm^{-1} range. Figure 2a shows the spectrum of the CaF$_2$/H$_2$O interface in the OH stretching region. It is compared with the spectra of two other
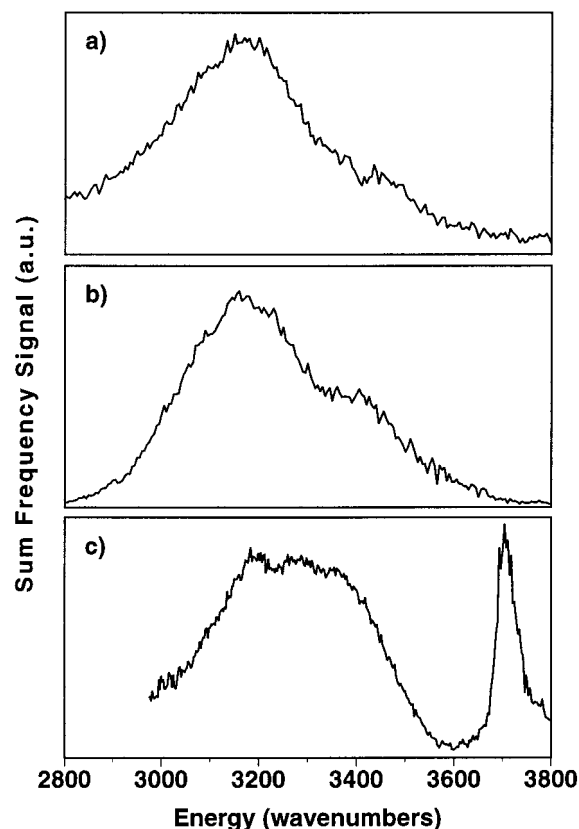
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Figure 2. Vibrational sum-frequency spectra (ssp polarization) of the (a) CaF$_2$/H$_2$O (pH 3.7), (b) SiO$_2$/H$_2$O (pH 5.1), and (c) air/H$_2$O interfaces.

interfaces studied in our laboratory using VSFS. Both the CaF$_2$/H$_2$O and SiO$_2$/H$_2$O interfaces (parts a and b of Figure 2) are characterized primarily by molecules in a highly ordered, tetrahedrally hydrogen bonded environment with a smaller response from more disordered, asymmetrically bonded water molecules. A spectrum of the air/H$_2$O interface (Figure 2c) shows contributions from water molecules in both of these bonding environments, as well as a large response from water molecules with uncoupled "free-OH" oscillators. The sensitivity of this technique to the interfacial water structure is shown well by the differing responses of these dissimilar interfaces.

The sum frequency spectra of the CaF$_2$/H$_2$O interface as a function of pH of the bulk aqueous phase are shown in Figure 3. The spectra show all three of the hydrogen-bonding environments mentioned above to varying degrees depending on the pH of the aqueous phase. At acidic pH, the spectra of the OH stretching region are dominated primarily by a band at 3160 cm^{-1}, with a minor contribution at ~3450 cm^{-1} which shows up as a shoulder on the edge of the primary peak. The spectrum at pH 2.9 (Figure 3a) indicates that water molecules at the CaF$_2$/H$_2$O interface are highly ordered and largely exist in a symmetrically bonded environment. Zeta potential measurements of this interface, which determine the interfacial potential at the plane of shear between the two phases, indicate that the surface of CaF$_2$ is positively charged over a large pH range.[17–19] The strong response at 3160 cm^{-1} can be attributed to the positively charged

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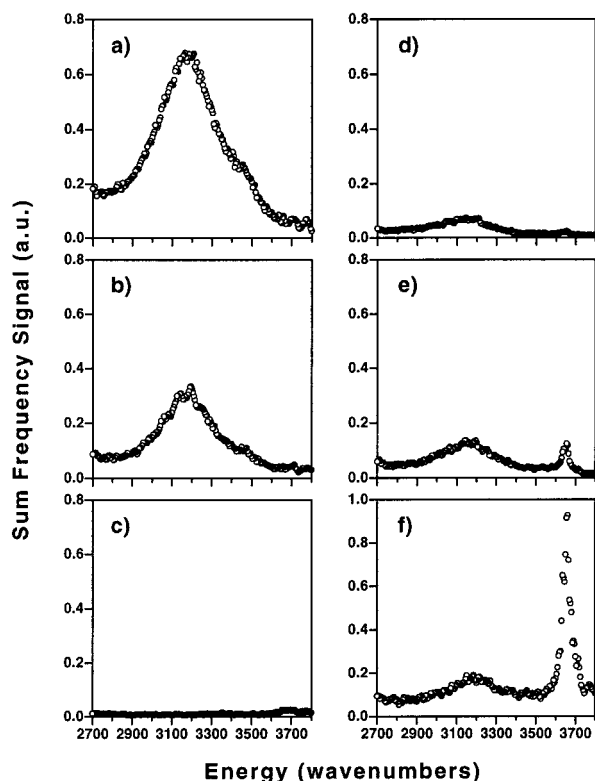
Figure 3. Vibrational sum-frequency spectra (ssp polarization) of the CaF_2/H_2O interface at pH (a) 2.9, (b) 5.1, (c) 6.4, (d) 9.3, (e) 12.3, and (f) 13.7.

CaF_2 surface orienting water molecules and facilitating the formation of a highly structured water phase at the solid/liquid boundary. The double layer established in the aqueous interfacial region also contributes to the strong signal due to a larger sampling depth created by the electrostatic field.[20] The surface charge of non-oxide solids such as CaF_2 can be understood as a preferential dissolution of surface ions[21] (fluoride ions in the case of CaF_2) over other charged ions. This leads to a deficiency of one ionic species on the solid surface resulting in a charged interface. In addition, the differing levels of hydration of the surface lattice ions will also contribute to generation of this surface charge.[22]

As the pH increases from 2.9 to 5.1 (Figure 3b), the sum frequency response decreases across the entire OH stretching region. We attribute this lower VSFS response from the interfacial water molecules to a decrease in the aligning force at the CaF_2 surface due to a decreasing charge at that surface. This results in a smaller electrostatic field experienced by water molecules above that surface and likely a fewer number of water molecules being aligned. As the solution near the interface becomes more bulklike (i.e., centrosymmetric), the allowed sum frequency response correspondingly decreases. It has been suggested previously[23] that the electric field due to a highly charged surface can align several layers of water molecules due to its semi-long-range nature. The fact that the sum frequency signal decreases as the pH is adjusted toward neutral indicates that at low pH the CaF_2 surface is highly

charged, but as the pH is increased toward neutral, this surface charge decreases. This phenomenon can be attributed to some type of specific adsorption of anions in solution (either OH^- or ClO_4^-) to the CaF_2 surface which decreases the field experienced by water molecules above that surface. Increasing the pH to 6.4 (Figure 3c) essentially reduces the sum frequency response to zero signal level. We attribute this lack of sum frequency response to a loss of the aligning force of the CaF_2 surface and a complete randomization of the water molecules above that surface. Streaming potential measurements indicate that the zero point of charge (ZPC) of CaF_2 is at pH 6.2,[24] which corresponds well with the loss of sum frequency signal observed near this pH. It should be noted that electrokinetic measurements of the zeta potential of the CaF_2/H_2O interface have determined that the point of zero *potential* occurs at approximately pH 9.[19] However, zeta potential measurements examine electrical properties at the plane of shear of the solid/liquid interface and can differ from the zero point of charge due to specific adsorption of ions to the solid surface.[25,26] Sum frequency response however, will be generated from molecules situated within the electric double layer, closer to the solid surface than the shear plane and therefore under different electric field conditions.

As the pH is increased above pH 6.4, the sum frequency spectra show evidence of the symmetrically hydrogen bonded water network returning to the interface, albeit at a lower total response than that of the acidic solutions. This trend continues as the pH is increased, with small increases in the strength of the well-ordered water signal. At pH 9.3 (Figure 3d), a peak at 3657 cm^{-1} begins to appear. This isolated, sharp feature continues to grow in as the pH of the aqueous phase is increased (Figure 3e), until at very high pH (pH 13.7), this feature essentially dominates the response from the OH stretching region of the spectrum (Figure 3f). The energy and width of this peak indicate that it arises from isolated, weakly hydrogen bonded OH oscillators, similar to the "free-OH" oscillator reported in other sum frequency studies.[13,14] The ion exchange properties of the hydrous CaF_2 surface have been studied by potentiometric titrations[6] and indicate that the ion exchange reaction between fluorine and hydroxide occurs to an appreciable degree beginning at pH 7–8 and dominates the surface chemistry above pH 11. Increasing the pH from neutral to basic drives the equilibrium of the ion exchange reaction of surface fluorine ions with OH^- ions in solution, or generated via the dissociative adsorption of water molecules on the CaF_2 surface, according to the reaction

$$CaF_2 + 2H_2O \Leftrightarrow Ca(OH)_2 + 2HF \qquad (1)$$
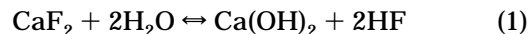
This results in a layer of weakly hydrogen bonded Ca–OH oscillators which are uncoupled from water molecules at the solid/solution boundary. This is a reversible exchange reaction, and by lowering the pH of our experimental solution into the neutral and acidic range, we are able to reproduce the spectra obtained from solutions with only acid additions. In addition, X-ray photoelectron spectroscopy studies of water adsorption on the $CaF_2(111)$ surface[27] have shown that the terminal

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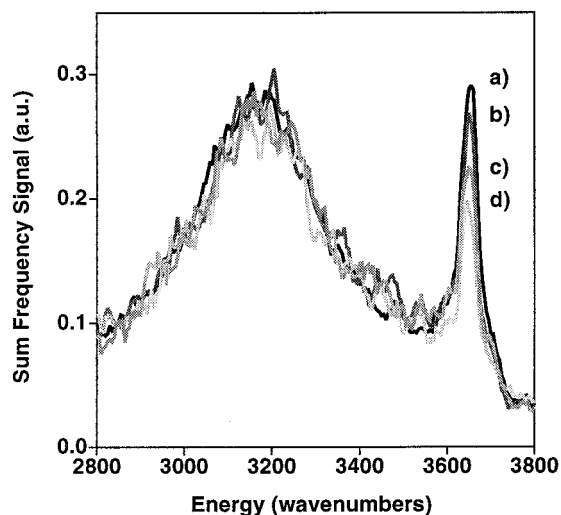
Figure 4. Vibrational sum-frequency spectra (ssp polarization) of the CaF$_2$/H$_2$O interface at pH 13.2 and (a) no added NaF, (b) 9.6×10^{-4} M, (c) 2.5×10^{-3} M, and (d) 1.0×10^{-2} M total NaF in solution.

fluoride ions of the (111) face are displaced by either hydroxyl groups and/or oxygen following the dissociative adsorption of water molecules at that surface, results which we qualitatively confirmed with some preliminary XPS studies.

To further study this ion exchange behavior, the CaF$_2$ surface was exposed to an aqueous solution of 0.15 M NaOH. The solution concentration of F$^-$ ions was then increased from 0 to 1.0×10^{-2} M by successive additions of NaF which should drive reaction 1 toward formation of CaF$_2$ at the expense of Ca(OH)$_2$. As shown in Figure 4a, the spectrum of the CaF$_2$/H$_2$O interface at pH 13.2 shows relatively strong responses at 3160 cm^{-1} from ordered, tetrahedrally bonded water molecules, as well as a strong, sharp response at 3657 cm^{-1} from the weakly coupled Ca$-$OH species. These additions result in a decrease in the sum frequency response from the weakly coupled OH oscillators at 3657 cm^{-1} as the F$^-$ ion concentration is increased (Figure 4b$-$d). In addition, there is little or no effect on the intensity or shape of the broad band at 3160 cm^{-1}, indicating that water molecules involved in this type of symmetrically bonded cooperative vibrational motion are not affected by the ion exchange reaction occurring among the F$^-$ and OH$^-$ ions at the solid surface.

Conclusions

We have conducted the first studies of water structure and ion exchange properties of the hydrous CaF$_2$/H$_2$O interface as a function of pH. Fundamental studies of the pH-dependent behavior of hydrous fluorite surfaces are essential for understanding the reaction mechanisms involved in calcium mineral flotation systems. At low pH, the positively charged CaF$_2$ surface facilitates the orientation of water molecules at the interface into a highly ordered, tetrahedrally coordinated state. The strength of the generated sum frequency signal implies that several layers of water molecules are influenced by this surface charge. As the pH is adjusted toward neutral, the charge of the CaF$_2$ surface decreases, resulting in a more random orientation of water molecules at the interface and a corresponding loss in the sum frequency signal. In the basic pH range, ion exchange of surface fluorine ions with hydroxide ions in solution or generated in the dissociative adsorption of water molecules, result in the formation of Ca$-$OH species on the solid surface. At very high pH, the Ca$-$OH species dominate the VSFS spectra. With an increase of the fluoride ion concentration in the high pH solutions, the ion-exchange process can be reversed to favor the formation of CaF$_2$ with a commensurate decrease in the weakly interacting OH stretch from Ca$-$OH.