

Investigations of the solid–aqueous interface with vibrational sum-frequency spectroscopy

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Abstract

Vibrational sum-frequency spectroscopy (VSFS) is increasingly being applied to understanding the molecular properties of the solid/liquid interface. There are many opportunities in the future for understanding important issues in interfacial science. This review provides insight into recent applications and advances of VSFS to the solid/aqueous interface with particular focus on the behavior of water at these interfaces, while highlighting some of the challenges and opportunities that lie ahead.

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1. Introduction

The solid–liquid interface, in particular, the solid–aqueous interface is of great importance in surface science. It is ubiquitous in both the environment and industry and arises in such varied examples as lubrication, oil recovery and corrosion [1,2]. The advent of techniques such as neutron reflectivity, surface electron scattering and nonlinear optical spectroscopies is allowing unprecedented access to these buried interfaces, and advances in these techniques, both experimental and computational, are allowing new interpretations of data and analysis of increasingly complex systems. Due to its ability to provide molecular level information about surface species with inherent discrimination against the surrounding centrosymmetric bulk media, vibrational sum-frequency spectroscopy (VSFS) is of particular value.

Vibrational sum-frequency spectroscopy typically makes use of two pulsed laser beams; one a fixed frequency visible beam and the other a tunable IR beam, that are

overlapped in space and time at an interface. The molecules at the interface will interact with the electric fields by generating a new field that oscillates at the sum of the incident frequencies; within the dipole approximation, this response is limited to those molecules in a non-centrosymmetric environment. By tuning the IR beam across a vibrational resonance, a significant enhancement of the signal is obtained. Because VSFS is a coherent process, the modes probed will have an associated phase which can cause interferences between modes, allowing orientation information to be obtained. Increasingly, this experimental information is combined with computer simulations to determine absolute orientations.

This review seeks to highlight some of the more recent work on the solid/aqueous interface done with VSFS. A more detailed treatment of VSFS can be found in any of a number of review articles and books [3–*10]. We have organized this review into a number of sections based on the various solids examined in contact with water. We begin with neat, non-metal aqueous interfaces and then discuss self-assembled monolayers, surfactants and adsorbates, polymers, ending with recent electrochemical studies.

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2. Neat solid–liquid interfaces

To understand the chemistry that occurs at solid/aqueous solution interfaces, it is vital to understand first the solid in contact with water. The findings of research into the behavior of water at solid oxides and salts are used to help interpret results from more complicated systems, such as those involving self-assembled monolayers (SAMs), surfactants and other adsorbates. While a number of neat solid/water systems have been investigated over the years with a variety of techniques, the number of systems investigated by VSFS remains small and is an active area of research.

Early work on the fused silica/water interface by Ong et al. [11] using second-harmonic generation (SHG), another surface-specific nonlinear optical technique, found that water is strongly oriented by the surface charge of the silica within the electric-double layer region. They were also able to confirm that silica has two types of silanol sites, each possessing a different pK_a . This work was followed by a VSFS study by Du et al. [12] whose goal was to elucidate the interfacial water species. They found that the water was dominated by two species, one tetrahedrally coordinated, located at 3200 cm^{-1} ; the other was found to be at 3450 cm^{-1} , indicative of water molecules in a more weakly associated hydrogen-bonding environment. The relative intensities of these peaks were found to change as a func-

tion of pH, and they proposed that the orientation of the interfacial water molecules flipped with increasing pH and surface charge.

The above work was recently revisited by the Shen group; their findings, although similar to those in reference [12] give significantly more detail about the interface. Fig. 1 shows VSFS spectra of the α -quartz and fused silica water interfaces [*13]. In both sets of spectra, the tetrahedrally coordinated and weakly bound water molecules are present; however, spectral fitting revealed that the tetrahedral peak was at a different frequency on quartz than on silica. The strongly coordinated water on α -quartz is 50 cm^{-1} closer to the location of the ice-peak at the ice/silica interface than that of the water/silica interface, indicating that water at the crystalline surface forms more ordered hydrogen bond networks. To further investigate the ordering of water at silica surfaces, the researchers performed a phase-sensitive VSFS experiment to experimentally determine the relative phases of the interfacial water peaks [14]. They found that at low pH, when the surface is almost neutral, that the strongly coordinated water and weakly coordinated water have different orientations; the water represented by the peak at 3200 cm^{-1} was oriented with its oxygen molecule pointed towards the surface. The asymmetrically bound molecules at 3400 cm^{-1} were found to be oriented with their H's pointed towards the surface. As they increased the solution pH, deprotonating the

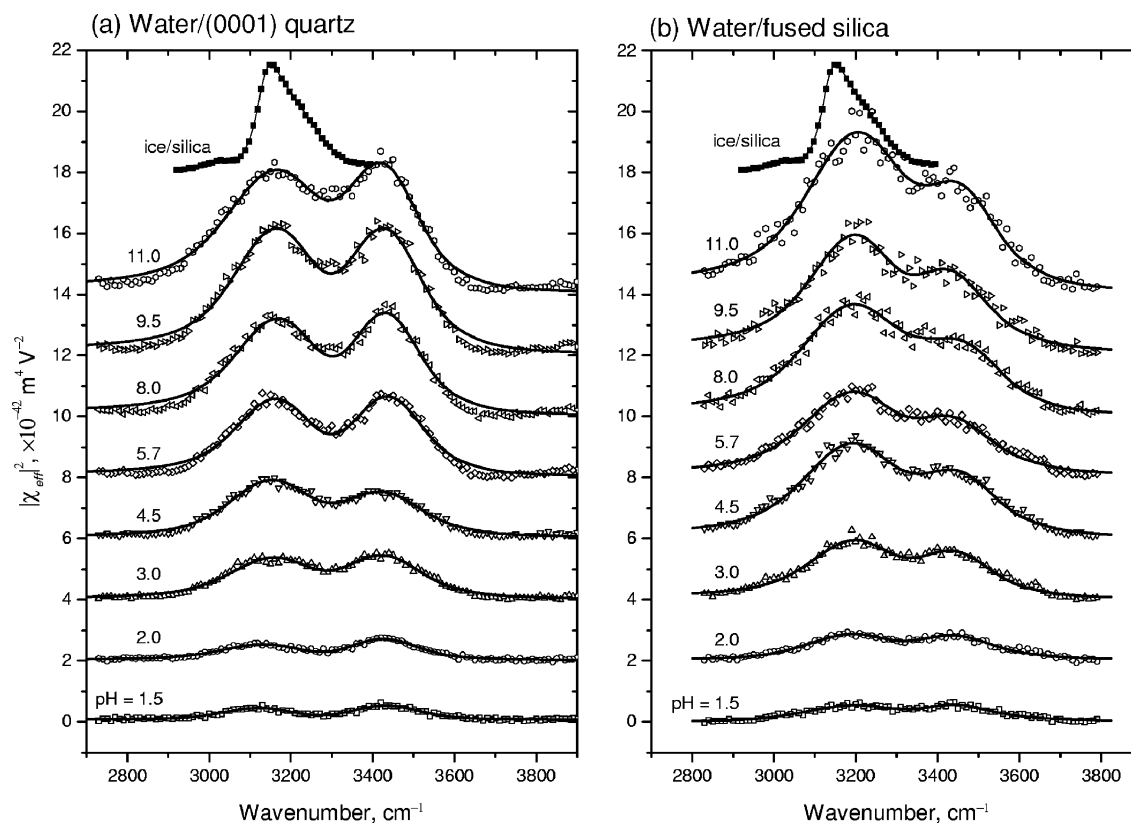


Fig. 1. VSFS spectra of the (a) water/ α -quartz (0001) and (b) water/fused silica interfaces. Both systems show the same pH behavior, but the water/quartz interface tetrahedrally coordinated peak is shifted to lower wavelength. The spectra are displaced in two unit increments (from [*13]).

quartz surface, less-coordinated water molecules increased in net orientation up to pH 4, while the strongly-bound peak showed no change until pH 4.5. At this point, the net orientation of these molecules begins to reverse; the process is complete by pH 9.5. These results suggest that there are two different protonation sites on the surface, one that is more easily deprotonated and one that is more difficult to deprotonate; in agreement with the conclusions of the SHG study [11].

Other oxide surfaces, such as titanium dioxide and sapphire, have been studied by VSFS in aqueous solutions. In 1999, Yeganeh et al. analyzed the behavior of water as it crossed the isoelectric point of sapphire [15]. They found both tetrahedrally coordinated and less coordinated water at the interface and that the VSFS signal intensity went through a minimum at pH 8, corresponding to the isoelectric point. From this, they concluded that the orientation of the interfacial water molecules reverses after passing this point. The titanium dioxide/water interface was recently studied by the Cremer group [16]. They found behavior similar to that of $\text{Al}_2\text{O}_3/\text{water}$, and concluded that the water orientation reversed after passing through the isoelectric point, at pH 5.5. This group also examined the effects of a sodium phosphate buffer on the interfacial water structure and found that it altered the water structure, increasing the intensity of the asymmetrically bound water relative to that of tetrahedrally coordinated water.

Oxide/water interfaces are not the only interface to have been studied by VSFS; fluorite (CaF_2), a slightly soluble mineral, has recently been examined by Becraft and Richmond [*17] at the water interface. Their experiments probed the interfacial structure and found that it was dominated by tetrahedrally coordinated water at low pH, and that this intensity decreased with increasing pH, up to the point of zero charge (PZC), pH 6.2 [18]. Continuing to

increase the pH, beyond the PZC resulted in an increase in the intensity of this water mode and an orientation change of the interfacial water molecules. They also observed that as pH approached 14, OH^- ions began to exchange with F^- ions at the surface, resulting in the appearance of a surface hydroxide with a sharp peak in the spectra at 3657 cm^{-1} . This substitution reaction could be driven back by adding excess fluoride ions.

3. Self-assembled monolayer/water interfaces

The interactions of water with covalently bound self-assembled monolayers (SAMs) are important in a number of fields [19–23], and there has been significant research into this area with VSFS. From the studies of the octadecyltrichlorosilane (OTS) SAM/water interface [24–*26] to the those of mixed SAMs [19,27,28] to work on amino [29,30] and (poly)ether terminated [31–33] monolayers, SAMs provide an ideal testing ground for obtaining molecular level detail on the interactions of water with technologically relevant materials.

The first monolayer to be studied by VSFS at a liquid interface was an OTS SAM; Guyot-Sionnest et al. looked at this system at the air interface and at the CCl_4 , methanol and hexadecane interfaces [24]. They found that the alkane chains were oriented very near to the surface normal in all the cases. This work was followed up by Du et al., who examined the water structure at the $\text{SiO}_2/\text{OTS}/\text{H}_2\text{O}$ interface [25] and observed a sharp resonance at 3680 cm^{-1} , indicating that water molecules at the monolayer surface sacrifice a hydrogen bond due to the hydrophobic interaction with the organic monolayer.

More recently, the $\text{SiO}_2/\text{OTS}/\text{H}_2\text{O}$ interface has been studied both in our group and by Uosaki [*26]. The spectra in Fig. 2 shows five major features found in our studies: the

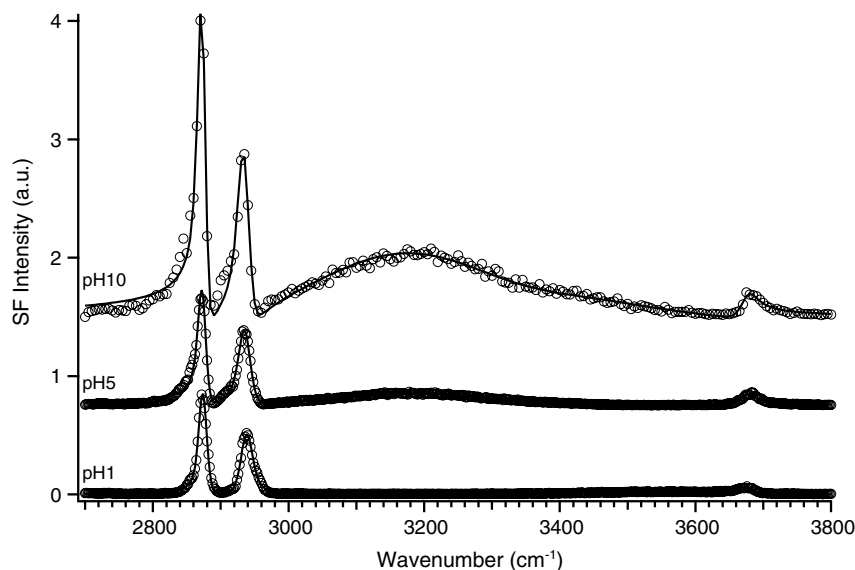


Fig. 2. VSFS spectra of the $\text{SiO}_2/\text{OTS}/\text{H}_2\text{O}$ interface (spectra are offset for clarity). At pH 1, below the PZC, there is very little water signal; at higher pH and surface charge, there are more oriented water molecules.

CH₃ Fermi resonance pair at 2875 and 2934 cm⁻¹, the strongly hydrogen-bonded and weakly hydrogen-bonded water peaks at ~3200 cm⁻¹ and 3450 cm⁻¹, respectively and the uncoupled OH oscillator at 3674 cm⁻¹. This last peak arises from water molecules exclusively at the terminus of the OTS monolayer and occurs when water molecules interact with the hydrophobic alkane chains and orient with one OH bond towards the surface and the other towards the aqueous phase. Its presence is indicative of a relatively sharp interfacial region, and has also been seen at the oil/water interface [34]. The methylene CH₂(ss) modes of the alkyl chain are absent in the spectrum and a very minor contribution from the antisymmetric stretch of the CH₂ moiety, indicating that the chains of the OTS molecules are in an all-trans configuration, with their terminal groups almost perpendicular to the interface, in agreement with previous studies [*26,27]. The tetrahedrally coordinated water region in the spectra shows behavior very similar to that of the fused silica/water interface, with the modes at 3200 cm⁻¹ and 3450 cm⁻¹ increasing growing in above a bulk pH of 5, while there is almost no signal in the water region below pH 5. This suggests that the water structure is dominated by the charging of the silica substrate; as the SiO₂ deprotonates and its electric field increases, water is increasingly preferentially oriented. At pH's lower than 5, the surface charge does not generate a sufficiently strong electric field to orient water molecules, which are at the end of the chains. Alternatively, this lack of signal may suggest that some water molecules are in contact with the silica surface and are oriented opposite to those at the end of the OTS chains, canceling out the signal [*26].

Other recent studies of the SAM/water interface have focused on terminal functionality. Recent work has examined the interface between an amino-terminated SAM and water [29,30]. The researchers coated a quartz prism with *N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane and varied the bulk pH in a phosphate buffer. They found the VSFS intensities were stronger at high and low pH than at intermediate pH's; findings that can only be explained by accounting for the ionization behavior of both the unreacted silanols and the amino groups. At high pH, the SiOH groups are deprotonated, resulting in a negative surface charge; while at low pH, these groups are protonated and neutral, the amino groups are positively charged and their electric field orients the water molecules. Intermediate pH's have less ordering because of lower surface fields. Another study examined the effect of water and CCl₄ on ethylene glycol terminated alkane thiols [32]. They found the monolayer to be well organized in air and that CCl₄ deformed both the chain backbone and the ethylene glycol headgroup. However, when the sample was exposed to water, it was determined that water was unable to penetrate into the undecane chain, but caused significant disorganization of the headgroup due to a favorable interaction with the oxygen atoms. In follow-up experiments these authors found that while exposure to water caused randomization,

removal of the SAM from water resulted in some water remaining in the ethylene glycol moieties forming bridging hydrogen bonds, but that all the water could be removed after exposure to vacuum [33]. These results and others [31] show that liquids perturb the structure of polar organic monolayers resulting in significant chain deformation in the presence of water.

There has been a great deal of VSFS research into thiol SAMs on gold and other metals, as well as work on Langmuir–Blodgett monolayers, but most of this work does not involve the monolayer/water interface.

4. Surfactants and adsorbates at solid/aqueous interfaces

Chemical and physical sorption of species at the solid–aqueous interface is of great theoretical and practical interest. Surfactant and polymer aggregate uptake on solid surfaces is important in the modification of surface properties for a number of relevant processes such as waste processing, petroleum recovery and mineral ore separation [2], and adsorption of these substances have been the focus of much VSFS research on both mineral [35–46], monolayer [47–52] and polymer surfaces [53,54]. Protein adsorption has received wide study [54–62], because of its importance in biomedical and food processing applications, where protein removal or adsorption prevention is critical [63,64].

Surfactant adsorption at the CaF₂/H₂O interface has been extensively studied [35–38]; the behavior of the neat interface has been discussed in a preceding section. Becraft et al. performed a series of experiments on the adsorption of sodium dodecylsulfate (SDS) to determine how this surfactant affects the interfacial water structure [*36,37]. In experiments performed at pH 5, below the PZC, such that the CaF₂ surface possesses a net positive charge, they found that a bilayer of SDS forms with increasing surfactant concentration. At low pH, monomer adsorption dominates the chemistry, as the anionic surfactant is attracted to the positively charged surface. The hydrocarbon tails of the molecules extend into the aqueous phase and disrupt the network of tetrahedrally coordinated water at the surface, resulting in a decrease in the VSFS intensity relative to that of the neat interface (Fig. 3a). As the surfactant concentration is increased, the surface charge on the fluoride is neutralized and a monolayer is formed; with the interface charge neutral, there is little to drive the orientation of interfacial water molecules, resulting randomization of the molecules and a loss of signal (Fig. 3b). Continuing to increase the surfactant concentration results in the formation of a SDS bilayer, as evidenced by a decrease in the CH₃ signal intensity in experiments performed in D₂O. As the bilayer forms, the interface reverses charge due to the buildup of negative charge at the surface and the water orientation reverses (Fig. 3c).

Becraft and Richmond also studied several carboxylate surfactants: (sodium) oleate, stearate, decanoate and hexanoate [38]. All of these surfactants showed the formation of

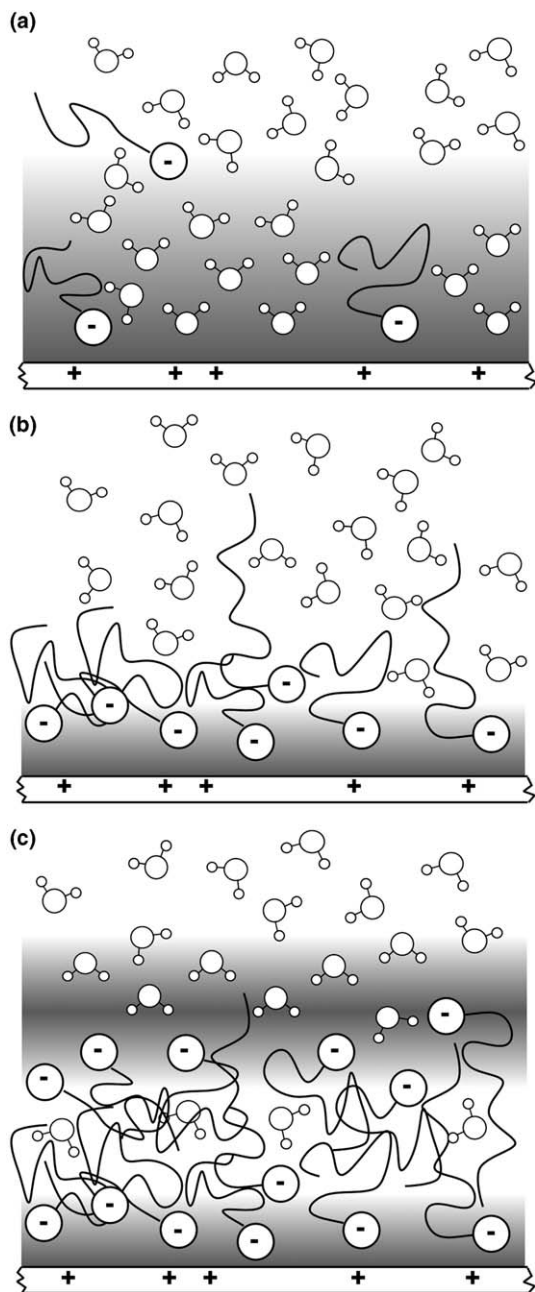


Fig. 3. Diagram of the three distinct adsorption regions of SDS on CaF_2 . (a) Monomer adsorption of anionic SDS to the positively charged CaF_2 surface, (b) the PZC of the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface and randomization of interfacial water molecule structure, and (c) bilayer formation and charge reversal at the $\text{CaF}_2/\text{H}_2\text{O}/\text{SDS}$ interface and the return of interfacial water structure above this layer. Reprinted with permission of the American Chemical Society from [*36].

a monolayer on the CaF_2 surface without the formation of a bilayer at high concentrations. The longer surfactants (oleate and stearate) formed tightly packed monolayers, and the stearate system formed a well-ordered monolayer, as evidenced by the appearance of an uncoupled OH peak at 3674 cm^{-1} . The decanoate and hexanoate system formed disordered monolayers, which was seen in the weak spectral response of the CH_3 modes, as well as the more signif-

icant intensity of CH_2 modes; this is likely due to a lack of significant van der Waals attraction between the molecules. All of these molecules passivated the surface charge of the fluorite and continued to pack onto the surface, reversing the electric field and thus the orientation of the water at the surface.

Kim et al. recently studied the adsorption of polydiallyldimethylammonium chloride (PDDA), a positively charged polyelectrolyte, at the silica/water interface [39]. They found that adsorption of PDDA had a significant effect on the interfacial water structure, with the surface charge being neutralized at pH 9.6, and water reversing its net orientation about this point. They also examined the effects of deposition conditions on the structure of the adsorbed layer; by altering the pH and PDDA concentration, they found the structure was more ordered at high ionic strength and pH, but was independent of bulk PDDA concentration. The Somorjai group recently looked at the alignment of three neutral polymers at this interface, but found no preferential orientation for any of them. The same polymer samples did show net polar orientation when deposited at the polystyrene/water interface [43].

There have also been numerous studies of protein adsorption at both the silica/water and polymer/water interfaces [54–62]. Work by Chen [58,59,61] and Somorjai [54,61] has focused on the adsorption of proteins on different surfaces, and how the protein orientation changes in different media. Research into protein adsorption on silica by Cremer has looked at the effect of this adsorption on water [55–57]. In a recent work studying human plasma fibrinogen adsorption on silica [57], this group found evidence that the arginine and lysine residues of the αC domain of the protein had net orientation at moderate pHs, where silica is negatively charged. This finding confirms the idea that the interaction of these domains with the central portion of the protein is electrostatic in nature.

5. The polymer/water interface

Another application of VSFS that has received considerable interest is the behavior of polymers at aqueous interfaces, particularly in comparison to the polymer interface with air. Because the performance of polymers can vary greatly depending on the environment, it is important to understand what is happening to these polymers at the surface. The studies in this area have examined resonances corresponding to either the components of the polymer backbone or side chains and give information about how the polymer restructures when it comes into contact with an aqueous environment [43,65–73]. Shifts in peak frequencies and changes in peak intensities of CH, CO and OH resonances, when comparing spectra taken in air versus in water, indicate different interactions and configurations of the polymer such as hydrogen bonding between the polymer and water molecules [74,75]. Chen et al.'s work on poly(ethyl methacrylate)

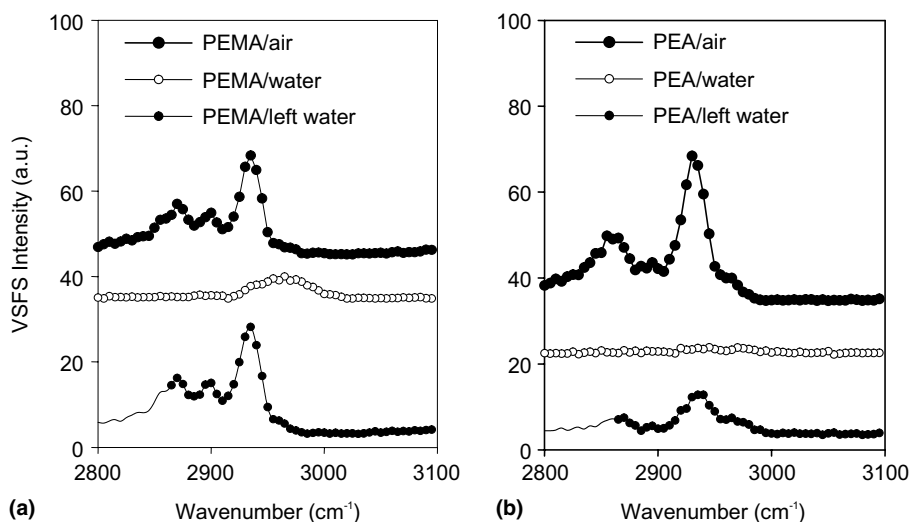


Fig. 4. PEMA (a) and PEA (b) are both strongly affected by the presence of water; both polymers become less organized upon exposure, but PEMA returns to its original configuration upon removal from water, showing structural reversibility (reprinted from Ref. [76] with permission of the PCCP Owner Societies).

(PEMA) and poly(ethyl acrylate) (PEA) in contact with air, water, and air after removal of water is an example of this application of VSFS represented in Fig. 4 [76]. The differences in VSFS signal when the polymers are exposed to water show that the methyl groups of the side chains are no longer oriented in the same direction as they were in the spectra at the interface with air. After removal of the water, the air/PEMA spectrum was recovered, suggesting that the restructuring is reversible for this polymer, while the continued lack of signal in the PEA spectrum shows that the reorganization is not reversible. The authors conclude that the polymers have undergone a restructuring due to the unfavorable interaction between the non-polar methyl groups and the water. In an earlier study on polymers with similar structures, the authors calculated the orientation angle distributions for the side chains from spectral data; they found the angular distribution to be broader at the air than at the water interface, proving that the polymer/water interface is more organized [*77].

6. The metal/aqueous electrolyte interface

VSFS has also been shown to be a powerful tool for studying metal electrode/aqueous electrolyte interfaces. The work summarized below focuses on determining the structure and orientation of the interfacial water molecules relative to the metal electrode. Peremans and coworkers investigated how water molecules orient at the gold electrode/electrolyte interface when a potential is applied [78]. Spectra in the OH stretching region show decreasing intensity with increased applied potential until the PZC is reached after which the intensity begins to increase with increasing applied potential. This indicates that as the potential becomes more positive, either the

interfacial water molecules were increasingly randomly oriented or the direction of orientation was closer to parallel to the surface giving a weaker VSFS response. From spectral fits, they determined that the water molecules were oriented with their oxygen atoms pointing toward the solution both in the potential region above and below the PZC, which is in contrast to previous studies [79]. This behavior is attributed to the interactions between the water molecules and the sulfate anions from the electrolyte solution, which are adsorbed on the gold electrode at more positive potentials, passivating the charge.

Work has also been done with platinum electrodes to elucidate the structure of water at the electrode/perchloric acid (electrolyte) interface. Zheng and Tadjeddine examined two stretching modes from the electrolyte solution that were assigned to hydrogen molecules adsorbed to the platinum electrode and ClO_4^- anions [80]. The authors conclude that the dependence of these signals on applied potential indicates that the signal indeed originates from molecules that are adsorbed on the platinum electrode. In addition to this evidence, the absence of significant OH stretch signal suggests that very few water molecules are present as adsorbates on the electrode. These authors also utilized the non-resonant VSFS signal response to applied potential in the absence of any OH resonance to reach this same conclusion in another study [81]. Baldelli et al. [82] also examined an aqueous electrochemical interface with a platinum electrode. VSFS spectra were taken of the platinum interface with 5 mole% water (D_2O)/acetonitrile mixed solvent with different 0.1 M MSO_3CF_3 salts ($\text{M} = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+, \text{and Cs}^+$) as a function of applied potential. As the applied potential becomes more negative (from -200 to -800 mV) and the surface becomes negatively charged, they concluded the D_2O displaces the

acetonitrile and orients with the oxygen end pointing toward the metal.

7. Conclusions

VSFS is showing promise in a number of fronts in understanding molecular interactions at the solid/liquid interface. Recent work has looked at the structure of water at several of solid surfaces and found that its behavior is dictated by the surface chemistry of the solid phase; it has also been seen that water can have a significant effect on the structure of adsorbates both through attractions and hydrophobic effects. However, there are many challenges and opportunities in the future. There is great interest in polymers and adsorbates at aqueous and non-aqueous liquid interfaces, and studies continue to improve as more groups are explicitly determining orientation information by coupling experimental data with computations, but new methods are needed to determine the effect of solvent molecules on the hyperpolarizability of a target analyte. There is also need to improve the modeling of the interfacial refractive index, to more accurately represent experimental spectra.

Much has been learned in the VSFS studies of electrochemical systems thus far but challenges remain. The often large non-resonant signals from these metallic and semiconductor surfaces make small signals difficult to isolate, but may also be used as an advantage for signal calibration and orientation. For bulk solid samples that are too thick to be transparent, one must approach the surface through a thin solvent layer to obtain data on adsorbing species. Opportunities abound for studies of dynamic processes at all timescales.

Recent advances have allowed the development of VSFS microscopy, which allows spatially resolved data collection; further development of this nascent technique is needed. In addition, the field of doubly resonant VSFS is beginning to be probed; this allows for significant enhancement of the VSFS signal, but requires additional data analysis due to the electronic excitation. Also, systems are now available that have pushed the bounds of VSFS to 16 μm , with more improvement possible as terahertz spectroscopy matures. A potential terahertz VSFS experiment would allow the probing of substrate–adsorbate bonds. In summary, we have highlighted some of the most recent work in VSFS at the solid/aqueous interface. The foundation for future work has been laid, with many opportunities ahead for studying the chemistry and physics of solid/liquid interfaces.

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