

Organization of Water Layers at Hydrophilic Interfaces

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Vibrational sum frequency spectroscopy (VSFS) has frequently been applied to the study of water structure at aqueous interfaces due to its ability to distinguish interfacial species in the presence of an overwhelming bulk contribution. Both hydrophobic (e.g., air–water,^[1–4] oil–water^[5]) and hydrophilic (e.g., quartz–water,^[6–11] monolayer–water^[12–15]) systems have been investigated. Generally, three OH stretch peaks are found at the hydrophobic interface at 3690, 3400, and 3200 cm^{-1} , while only the lower two are observed in the hydrophilic case. The 3690 cm^{-1} feature, which is caused by a free OH stretch at the interface, is fairly narrow. By contrast, the 3200 cm^{-1} peak is often quite broad and due to water molecules with a full complement of hydrogen bonds in a tetrahedral arrangement. This feature occurs at the same frequency as the bulk infrared absorption of ice.^[16] The peak at 3400 cm^{-1} is also broad and assigned to water molecules with either asymmetric hydrogen bonds or bifurcated hydrogen bonds. This resonance is found at approximately the same frequency as the infrared absorption of water molecules in the bulk liquid and, hence, represents incomplete or more disordered hydrogen bonding.

Despite the large number of VSFS studies that have been performed, only the location of species that give rise to the 3690 cm^{-1} feature is known with any certainty. In this case, the species are believed to be directly adjacent to the hydrophobic medium with the non-hydrogen-bonded OH group pointing up into it.^[1] The lack of information on the other two species is unfortunate, as the assignment of their relative locations would greatly aid in a comprehensive understanding of interfacial water structure and bonding. The goal of the present work, therefore, is to help ascertain the relative interfacial locations of the species that give rise to the 3200 cm^{-1} and 3400 cm^{-1} VSFS signals. It was reasoned that detailed information could be gleaned at well-defined hydrophilic interfaces, such as those between an eicosanoic acid monolayer and bulk aqueous solution. Divalent metal cations adsorbed at this surface have been observed to alter many of the properties of the organic thin film including its average molecular area, stiffness and phase behavior.^[17–19] Species such as Zn^{2+} ions bind strongly to the carboxylate headgroups while Mg^{2+} ions are more weakly associated. This fact should almost certainly afford the various M^{2+} ions differing abilities to perturb the water layers most closely associated with the monolayer headgroups. The strategy employed here was to monitor VSFS spectra at various concen-

trations of the divalent metal ions to determine their effects on water structure.

VSFS spectra obtained from eicosanoic acid monolayers (surface pressure (π) = 30 mN m^{-1}) spread on subphases containing 1 μM of each of the two divalent cations are shown in Figure 1. Sufficient NaOH was added to each system to bring the

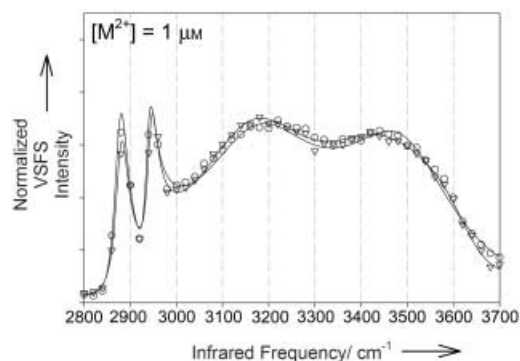


Figure 1. VSFS spectra of an eicosanoic acid monolayer spread at the air/water interface taken with the ssp (s-Sum Frequency, s-Visible, p-Infrared) polarization combination. The subphase M^{2+} concentration used was 1 μM . Spectra taken in the presence of Mg^{2+} ions are represented by \circ while those obtained in the presence of Zn^{2+} ions are represented by ∇ .

pH value to 10, which forced complete deprotonation of the monolayer headgroups.^[20] In addition to the OH stretch peaks at 3200 and 3400 cm^{-1} , two CH_3 resonances at 2890 and 2950 cm^{-1} from the methyl terminus of the monolayer's alkyl chains were also observed. Their presence, and the lack of features for methylene stretches, was indicative of a well-ordered monolayer at the interface.^[21] Spectra from monolayers at lower cation concentrations showed only negligible differences from those in Figure 1. This result was in agreement with the notion that only minimal absorption occurred at this concentration.^[22–24]

Dramatically different spectra were obtained when the divalent cation concentrations were increased to 10 μM (Figure 2). The Mg^{2+} ions gave rise to less overall signal attenuation. In this case the 3400 cm^{-1} feature was somewhat larger than

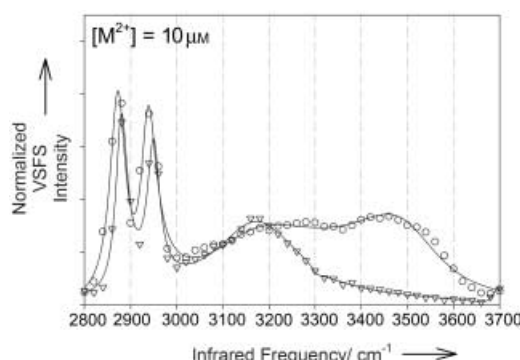


Figure 2. VSFS spectra of an eicosanoic acid monolayer spread on basic subphases containing 10 μM M^{2+} ($\text{M} = \text{Mg}, \text{Zn}$). Spectra taken in the presence of Mg^{2+} ions are represented by \circ while those obtained in the presence of Zn^{2+} ions are represented by ∇ .

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that at 3200 cm^{-1} . On the other hand, the spectrum of the system with Zn^{2+} ions showed little evidence of any signal at 3400 cm^{-1} .

These experiments were repeated at $100\text{ }\mu\text{M}$ of each cation (Figure 3). As can be clearly seen, this concentration had little additional effect on the overall spectra other than to further

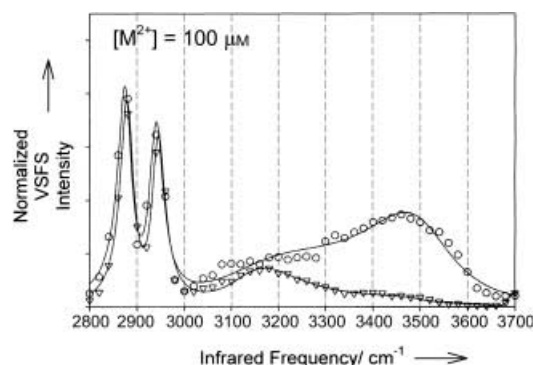


Figure 3. VSFS spectra of an eicosanoic acid monolayer spread on basic subphases containing $100\text{ }\mu\text{M M}^{2+}$ ($M = \text{Mg}, \text{Zn}$). Spectra taken in the presence of Mg^{2+} ions are represented by \circ while those obtained in the presence of Zn^{2+} ions are represented by ∇ .

attenuate the 3200 cm^{-1} feature in each case. This small additional attenuation was probably the result of enhanced charge screening in the double layer. Indeed, it has been previously demonstrated that the 3200 cm^{-1} feature often correlates well with the interfacial potential, while the 3400 cm^{-1} feature has not displayed this behavior.^[7, 9–11] Furthermore, it has been previously shown that high surface coverages of divalent metal cations at the monolayer interface already occur by $10\text{ }\mu\text{M}$.^[22–24]

The major differences in the ions' interactions with the monolayer are in their modes of binding. In the case of Zn^{2+} ions, the divalent metal cation binds directly to the carboxylate, which acts as a bidentate chelator.^[25] On the other hand, Mg^{2+} has been shown to have a more ionic interaction with carboxylates, which should allow the headgroup hydration to remain intact.^[26] We therefore propose that the 3400 cm^{-1} feature in these VSFS spectra comes from water molecules adjacent to the monolayer that are involved with the solvation of the headgroups. This conclusion is based on the fact that the 3400 cm^{-1} feature is much more strongly attenuated by the presence of Zn^{2+} , whose coordination is expected to displace even the last solvation shell associated with the monolayer. On the other hand, the 3200 cm^{-1} peak is not associated with water molecules directly bound at the headgroup, but rather with species in subsequent water layers.

The assignments of these modes are consistent with the fact that the 3400 cm^{-1} peak is associated with species that may contain only two or three hydrogen bonds to other water molecules,^[27] while the 3200 cm^{-1} peak more closely matches that of bulk ice.^[27] The frustrated hydrogen bonding of the interface-adjacent structure is not surprising in light of the geometric constraints (e.g., lattice mismatch) for hydrogen-

bonding water to carboxylate headgroups.^[1, 12] On the other hand, the ability of subsequent layers to align is almost certainly related to the magnitude of the interfacial potential and the length over which it is screened.^[7, 9–11] We strongly suspect that other systems, including the quartz/water interface, will probably correspond generally to the model stated above. Namely, water molecules immediately adjacent to the hydrophilic interface have fewer hydrogen bonds and are the major contribution to the 3400 cm^{-1} signal. Additionally, any subsequent layers that still do not display the isotropic characteristics of bulk water will have tetrahedral bonding. This suggestion is based on the fact that many other hydrophilic interfaces also lead to substantial lattice mismatch for hydrogen bonding to adjacent water molecules.

Experimental Section

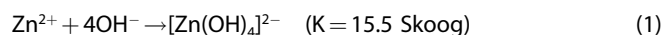
VSFS experiments required a fixed frequency visible beam and a tunable infrared source. The radiation was produced with a passive-active mode locked Nd:YAG laser (PY61c, Continuum, Santa Clara) equipped with a negative feedback loop, that was used to pump an optical parametric generator/oscillator (OPG/OPA) stage (Laser Vision, Bellevue, WA). The OPG/OPA output a visible beam at 532 nm , and a IR beam tunable over the CH and OH stretch regions of the vibrational spectrum ($2800\text{--}3800\text{ cm}^{-1}$). After the OPG/OPA, the two beams were temporally and spatially aligned at the sample stage. The intensity of the sum frequency signal was monitored, with a photomultiplier tube (R647, Hamamatsu, Japan), as a function of the frequency of the infrared input. The signal was sent to a gated integrator (SR250, Stanford Research Systems, Sunnyvale, CA) and its intensity was recorded on a computer. After data acquisition and background subtraction, the spectra were normalized to the signal from a piece of z-cut crystalline quartz.

All VSFS experiments reported herein were performed at the air–water interface of a Langmuir trough. The trough (Model 601M, Nima Technology Ltd., Coventry, England) used in these experiments monitored and controlled the lateral pressure of the fatty acid monolayers with a Wilhelmy plate and Teflon barriers. The monolayers were placed atop various aqueous subphases, prepared from high purity salts (Aldrich) and dissolved in deionized water ($>18\text{ m}\Omega$) to make stock solutions. Subphases of different cation concentrations were made by serial dilution. Each solution was then adjusted to $\text{pH } 10 \pm 0.1$ by the addition of an appropriate amount of concentrated NaOH and used within two hours of pH adjustment.

Basic subphase pH values were required to ensure that the monolayers would fully deprotonate.^[20] As a result of the high hydroxide concentrations, the zinc solutions represent supersaturated conditions ($\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2$). Despite this, the Zn^{2+} ions do not precipitate out of solution during the time of the experiment. All salt solutions were adjusted to basic pH immediately before spectroscopic investigation and used within a maximum of 2 h. Two experiments were performed in our lab in order to verify the assertion that no precipitate was formed within the time required for spectroscopic investigation. First, a freshly prepared zinc solution was sealed in a container with a pH probe, which was used to monitor the pH change of the solution over time. The formation of zinc hydroxide over time should result in a decrease in the pH value of the solution as the hydroxide ions precipitate out. It took more than 12 h to see the pH fall by just 0.2 units. Second, a freshly prepared zinc solution was monitored with dynamic light scattering

in an attempt to observe the formation of precipitate particles in solution. No particles were observed over the first 10 h after solution preparation. It should be emphasized that these controls were for worst case scenarios. In our VSFS experiments, we immediately placed the solutions in contact with the fatty acid monolayer. Since ions are quickly recruited to the interface, there are actually many fewer ions in bulk solution under experimental conditions.

Finally, another equilibrium [Eq. (1)] must also be considered. Zinc ions are in fact amphoteric and at high hydroxide concentrations:



Therefore, it is not expected that ions will precipitate out of solution in the experiments we present here.

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Additivity Effects in the Reactivities of Bimetallic Cluster Ions Pt_mAu_n^+

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Introduction

Understanding composite properties of chemical compounds forms a long-standing goal. A classic example which illustrates how to tackle this problem is Pauling's seminal proposal of the electronegativity scale.^[1] A comparison of the bond-dissociation energies of diatomic molecules X_2 , XY , and Y_2 revealed enhanced stabilities of the heteroatomic compounds. Pauling explained this synergistic effect by the introduction of the electronegativity concept. This far-reaching interpretation only became possible because the chosen systems were simple enough to exclude any additional, potentially obscuring effects.

In principle, the approach of comparing diatomic compounds can be transferred to any other problem related to the origin of composite properties. However, by no means do all conceivable combinations of elements from the periodic table give diatomic molecules that are sufficiently stable to be handled in bulk quantities at ambient temperatures. This holds particularly true for the d-block elements which occur in the metallic state at normal conditions. For these elements, only gas-phase techniques permit the in-depth investigation of well-defined molecular systems under rigorous exclusion of any environmental effects.

Very recently, we applied this methodology to the behavior of the cluster ions Pt_2^+ , PtAu^+ , and Au_2^+ in C-N coupling processes.^[2] In many respects, the reactivity of the bimetallic species appeared intermediate between those of Pt_2^+ and Au_2^+ , and thus promises to act as an interesting example of additivity effects beyond the scope of C-N coupling. Herein we further explore this issue and also consider larger clusters up to the tetramers Pt_mAu_n^+ ($m+n=4$). The inclusion of the larger systems allows stepwise variation of the cluster composition and might reveal size-specific effects as well. The reactivities of the clusters are exemplarily probed by their reactions with dioxygen and methane, which both behave differently towards homonuclear Pt_m^+ and Au_m^+ clusters.

Results

Generation of the cluster ions from a 1:1 platinum-gold alloy (see Experimental Section for details) yields a mixture of Pt_mAu_n^+ ions. The small mass difference between Pt and Au results in isobaric interferences. For example, $^{195}\text{Pt}^{197}\text{Au}^+$ as the most abundant bimetallic dimer is overlapped by $^{196}\text{Pt}_2^+$ and $^{194}\text{Pt}^{198}\text{Pt}^+$. As the difference between the exact masses of these ions lies in the

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