Potential-Dependent Vibrational Spectroscopy of Solvent Molecules at the Pt(111) Electrode in a Water/Acetonitrile Mixture Studied by Sum Frequency Generation

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Abstract: Sum frequency generation (SFG) vibrational spectra of D_2O and/or acetonitrile (CH_3CN) on a Pt(111) single-crystal electrode were obtained as a function of applied potential in a 5 mol % water/acetonitrile mixed solvent with different 0.1 molar MSO_3CF_3 salts ($M = H^+$, Li^+, Na^+, K^+, and Cs^+). The results provide a very specific model for the composition of the inner Helmholtz layer as a function of potential and surface charge. Acetonitrile dominates the inner layer with the CN group directed toward the metal at potentials where the metal has a positive charge. As the surface becomes negatively charged, the acetonitrile orientation flips 180°, with the CH_3 group pointing toward the surface. At even more negative surface charge, D_2O displaces acetonitrile from the inner layer and is the predominant molecule on the surface. Here water is present as an oriented molecule with the oxygen end pointing toward the metal. The potential (and surface charge) where water is the dominant molecule in the inner Helmholtz layer is determined by the solvation energy of the cation.

Introduction

The properties of the solid−liquid interface are controlled in large part by potential and charge. To obtain molecular details of this interface the use of spectroscopic methods proves to be extremely beneficial.[1−3] In this study, sum frequency generation (SFG) is used as a vibrational spectroscopic probe of the structure of solvent molecules adsorbed at the Pt(111) electrode. SFG is an ideally suited technique since as a $\chi^{(2)}$ spectroscopy it will, in the electric dipole approximation, only detect molecules in a noncentrosymmetric environment. Therefore, the peaks in a SFG spectrum are due to molecules at the interface that have a preferential orientation along the surface normal, and molecules in the bulk solution that are randomly oriented do not give rise to a sum frequency signal. This permits the selective investigation of the relatively few surface molecules even in the presence of an overwhelming number in the bulk solution. In this study, we used a 5 mol % water/acetonitrile mixed solvent and found that either water or acetonitrile (CH_3CN) is the dominant molecule in the inner Helmholtz layer, depending on the electrode potential and the surface charge. Acetonitrile dominates the surface coverage with the CN group directed toward the metal at potentials where the metal has a positive charge, at +400 to 1200 mV vs Ag/AgCl. As the surface becomes negatively charged (at −200 to +400 mV), the acetonitrile orientation flips 180°, with the CH_3 group predominantly pointing toward the surface. At even more negatively charged surfaces, D_2O begins to displace acetonitrile from the surface and is the predominant molecule on the surface at −200 to −800 mV (vs Ag/AgCl). The potential where water is the dominant molecule at the surface is determined by the solvation energy of the cation, i.e., the more strongly solvated the cation the lower the potential for oriented water to form at the surface.

Experimental Section

SFG spectroscopy is performed using a thin-layer electrochemical cell that has been described in detail elsewhere.[4] The cell is equipped with a Pt(111) working electrode, Pt wire counter electrode, and a Ag/AgCl reference electrode. The experiment involves spatially and temporally overlapping a tunable infrared and fixed frequency visible laser beam on the surface of the electrode. The generated sum frequency that occurs at the metal electrode is spectrally filtered and detected with a photomultiplier tube. The energy densities are 3 and 10 mJ/cm^2 for the 532 nm and infrared beams, respectively.

The only significant SFG signal is generated at the metal/solution interface. This is evident by the dependence of the SFG signal on electrode potential, on the polarization of the light fields, and on the thickness of the layer of trapped electrolyte. All spectra presented here are taken with ppp polarized laser beams (p-sum frequency, p-visible, p-infrared). Some SFG signal from acetonitrile or D_2O at the CaF_2 window is seen with ssp polarization at higher beam energies (532 nm = 30 mJ/cm^2 and infrared = 20 mJ/cm^2), but the signal is about $^1/_3$ of that from the metal with ppp polarization using the beam energies given in the previous paragraph. No SFG signal is seen with ppp polarization

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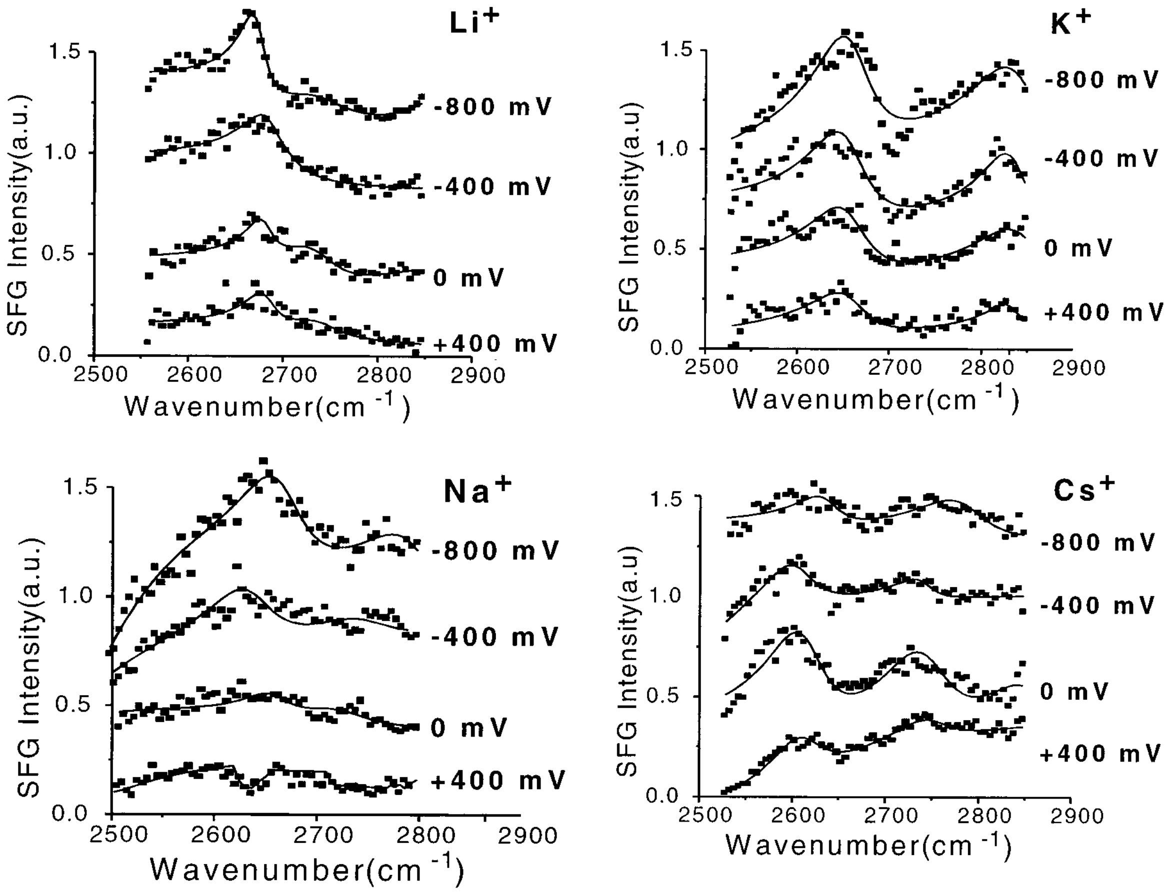

Figure 1. SFG spectra of OD vibrations for 5 mol % D_2O in acetonitrile solution on Pt(111) as a function of potential. The electrolyte is 0.1 M MSO_3CF_3 (M = Li, Na, K, Cs). Potential is with respect to a Ag/AgCl reference. Lines are a curve fit from eq 2.

from the window/solution interface using the lower beam energies. If the solvent layer between the electrode and window is more than ca. 0.5 mm thick, the infrared light is completely adsorbed and does not reach the electrode surface, and no SFG signal is detected. Only ppp spectra will be presented here to ensure there is signal from only the Pt surface.

The solutions used here are 5 mol % D_2O in acetonitrile prepared volumetrically. Alkali triflate salts were prepared by mixing the alkali hydroxide, MOH (M = Li^+, Na^+, K^+, Cs^+) ,with triflic acid, HSO_3-CF_3. All reagents were purchased from Sigma-Aldrich and used without further purification. The solutions are 0.1 M salt in 0.05× (mole fraction) D_2O/acetonitrile. All other experimental details are presented in a previous publication on the Pt(111) electrode in acetonitrile/water mixtures.[5]

Background

The SFG process involves three photons, two input beams and one output.[6-8] The output signal is coherent and directional, based on phase matching conditions.[9] The polarization of the beams can be varied independently to access different components of the susceptibility tensor. The SFG signal intensity, I_{SF}, is related to the second-order macroscopic susceptibility, $\chi^{(2)}$, by

$$I_{SF} \propto |P^{(2)}|^2 = |\chi^{(2)}:E_{vis}E_{IR}|^2 \qquad (1)$$

where P is the induced polarization in the surface layer and E_{vis} and E_{IR} are the electric fields of the visible and infrared beams, respectively. The susceptibility contains resonant and nonresonant components that interfere with each other. This interference depends on the magnitude and phase of the two components and can produce complex line shapes in a SFG spectrum.[9-11] Qualitatively, the intensity in an SFG spectrum depends on the orientation of the functional group (only the component of the transition dipole projected along the surface normal is detected), the square root of the number of molecules contributing to the signal, and their infrared and Raman cross-sections.

To extract relative peak intensity information about D_2O adsorbed at the platinum surface the spectral analysis of the SFG spectra was performed as follows. Each spectrum was fit to eq 2, where $\chi^{(2)}$ is the

$$\chi^{(2)} = \chi_R^{(2)} + \chi_{NR}^{(2)} = \chi_{NR}^{(2)} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma} \qquad (2)$$

second-order susceptibility, A_q is the mode strength, ω_{IR} and ω_q are the infrared frequency and normal mode vibration, respectively, and Γ is the damping factor for the vibration.

Typically two resonant modes and a nonresonant background, $\chi^{(2)}_{nr}$, were included, e.g. the symmetric (ν_1) and asymmetric (ν_3) OD vibration of D_2O and a broad background feature. The fitting of methyl resonances in the CH region was described in detail previously.[5]

Results

The SFG spectra in the OD stretching region are shown in Figure 1 as a function of potential and electrolyte. The OD peak

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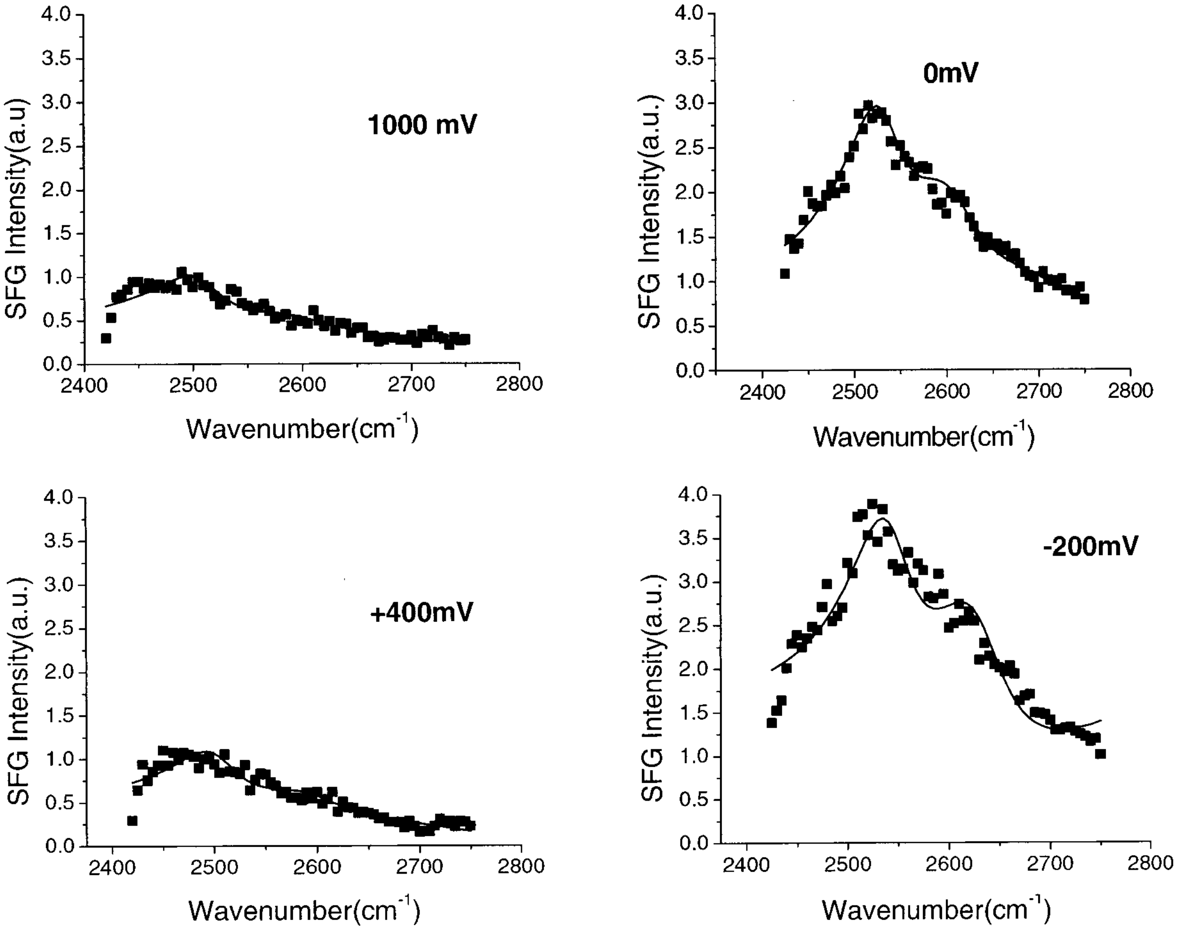

Figure 2. SFG spectra of OD vibrations of 5 mol % D_2O in acetonitrile solution as a function of potential. The electrolyte is 0.1 M HSO_3CF_3. Potential is with respect to a Ag/AgCl reference. Lines are a curve fit from eq 2.

shows a strong intensity at negative potentials, e.g. below −200 mV vs Ag/AgCl. Depending on the type of electrolyte used, the peak intensity appears at different potentials, as seen in Figure 1. The only two peaks seen are at ∼2680 and ∼2800 cm^{-1}; no intensity is noted in the lower wavenumber (∼2200−2550 cm^{-1}) region where water OD peaks with hydrogen bonding are expected. D_2O peaks generally become more narrow, blue-shifted, and intense as the potential becomes more negative. Peak width for the D_2O resonances is about 30 cm^{-1}; this is comparable to that measured in bulk acetonitrile−water solution with infrared spectroscopy.[12] Qualitatively, the two peaks in the spectra have the same potential dependence for their intensity and frequency shift. For the Li^+, K^+, and Na^+ cations the maximum intensity is at −800 mV while for Cs^+ it reaches a maximum near −200 mV, and then decreases at lower potentials. The same qualitative features were observed in the OH region with H_2O as the solute. However, due to the effect of atmospheric water on the absorption of the incident infrared beam, these results were not used.

Results with triflic acid (hydronium as cation) are shown in Figure 2. The OD peaks are at 2530 and 2620 cm^{-1}. The intensity in this region reaches a maximum at −200 mV. Spectra could not be obtained below − 200 mV due to H_2 evolution from the Pt. The vibrational features are reversible between −200 and +1000 mV.

The SFG spectra in both the CH stretching and OD region are presented in Figure 3 for 0.1 M $LiSO_3CF_3$ electrolyte. At more positive potentials, two features are seen at 2950 and ∼3000 cm^{-1} that are due to the symmetric and asymmetric stretching vibrations of acetonitrile,[13] while no distinct peak is observed in the OD region. As the potential becomes more negative, the peak at 2950 cm^{-1} turns into a dip in the spectrum at about 2930 cm^{-1} and the D_2O features appear at 2680 and 2750 cm^{-1}. The features in the CH region become weak as the potential goes below −200 mV vs Ag/AgCl. At even more negative potentials, the OD peaks become more prominent reaching a maximum at −800 mV. The features in the CH and OD regions are reversible for several cycles of the potential between −800 and +1200 mV, after which all peaks lose intensity. Apparently there is some decomposition of acetonitrile at the potential limits leading to contamination of the electrode surface. The general features in the spectra were similar for D_2O concentrations up to 20 mol %. However, the spectra became noticeably noisier for concentrations above 10 mol %. The CH spectra of acetonitrile are insensitive to the identity of the cation (except for H^+, discussed below) and have the same potential dependence.

Discussion

Sum frequency generation allows the study of the vibrational spectra from molecules adsorbed at the metal/solution interface without contributions from the same molecules in the bulk solution. The first characteristic to be noticed about the spectra in Figure 1 is the presence of only two relatively narrow peaks. These features are at ∼2650 and ∼2750 cm^{-1} and are assigned

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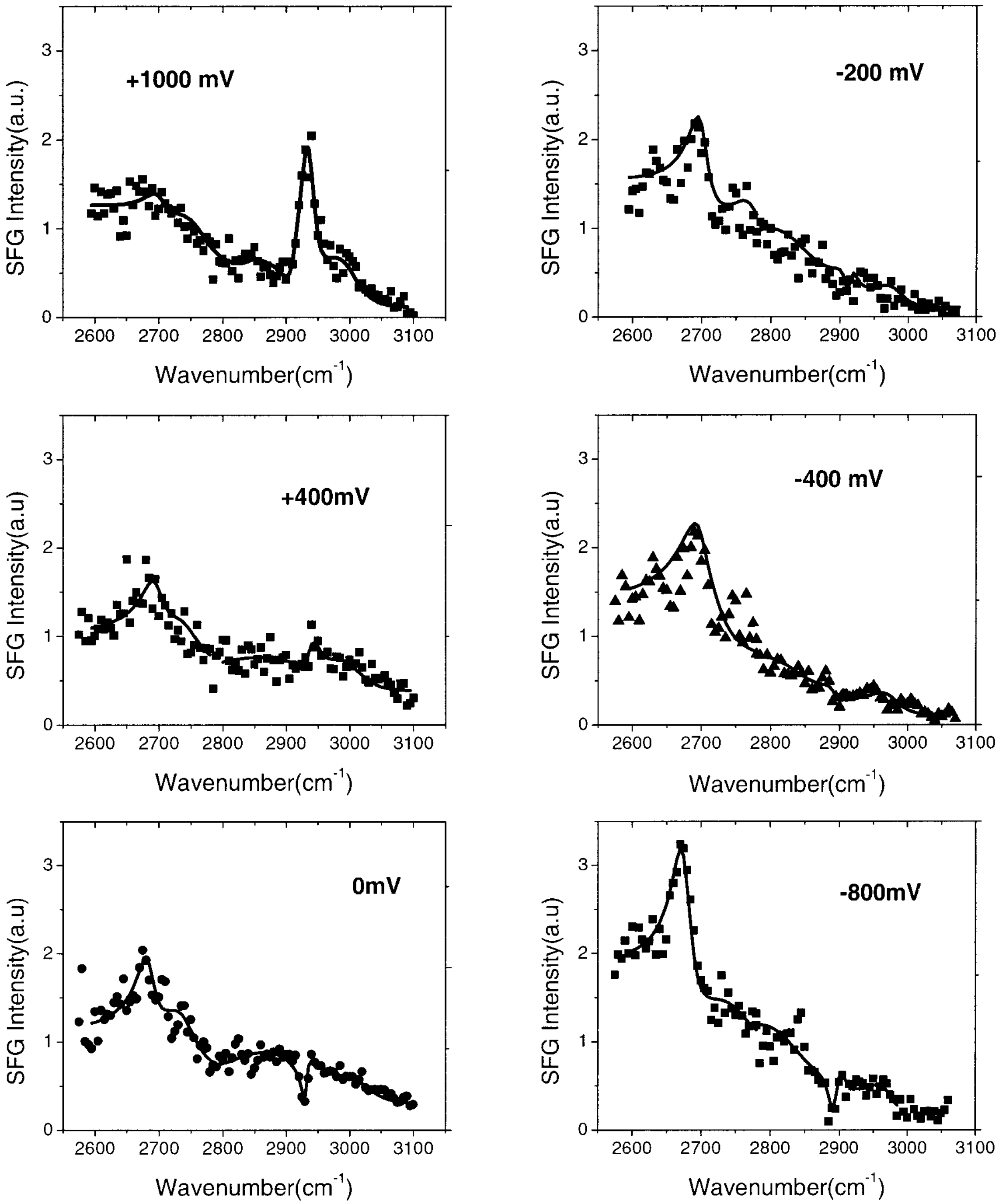

Figure 3. SFG spectra for 0.1 M $LiSO_3CF_3$ in a 5 mol % D_2O−acetonitrile mixture as a function of applied potential (vs Ag/AgCl). The line is the curve fit from eq 2.

to the free OD stretching vibrations of D_2O, ν_1 and ν_3, the symmetric and asymmetric stretches, respectively.[14] The peak positions are close to the OD symmetric stretch vibrations of a free D_2O molecule in the gas phase.[13] This indicates that the OD oscillators are not hydrogen bonded, and are not similar to the free OH seen on liquid water surfaces observed with SFG,[15,16] where only one OH group is pointing out of the surface. The peak is broadened (~30 cm^{-1}) relative to the gas-phase peak, and is likely due to interactions with the acetonitrile solvent or the metal surface.[12,17] The OD peak frequency indicates that both OD bonds are pointing away from the surface with the oxygen toward the metal (state III in Figure 4). The low concentration of D_2O used here (5 mol %) does not allow an extensive hydrogen-bonded network to form that results in peaks only in the high wavenumber region of the vibrational spectrum. Compared to liquid water/air and ice/air surfaces,[16,18,19] the D_2O molecules are isolated from neighboring D_2O molecules on the platinum surface. The precise frequency position of the peak is different for the different cations. The ν_1 is about 2675 cm^{-1} for Li^+ and Na^+, 2650 cm^{-1} for K^+,

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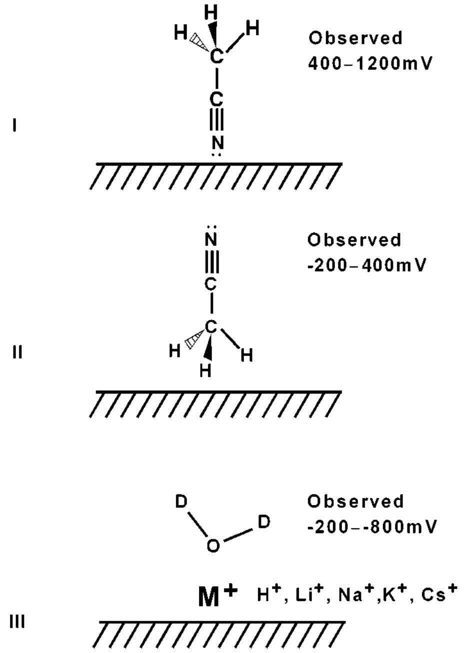

Figure 4. Molecule adsorption on the Pt(111) electrode at different potentials. Potential scale is with respect to a Ag/AgCl reference.

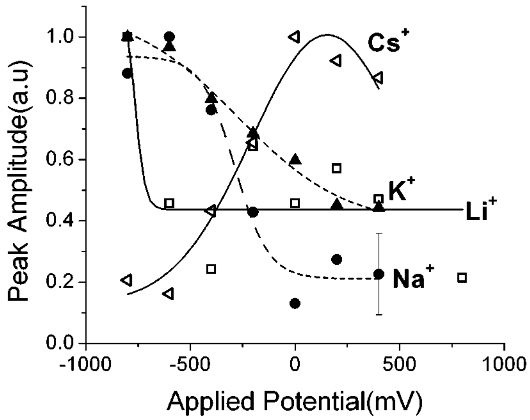

Figure 5. Peak amplitude for ν_1 in D_2O in different electrolytes: (□) Li^+, (●) Na^+, (▲) K^+, and (△) Cs^+. Potential is with respect to a Ag/AgCl reference.

and shifts to 2600 cm^{-1} with Cs^+. There is a peak at ~2750 to 2800 cm^{-1} due to the asymmetric stretch of D_2O, but the more complex line shapes and weak signal, however, limit the utility of this vibrational feature. The potential dependence of the peak amplitude for ν_1 of D_2O for the different cations is summarized in Figure 5. The intensity is normalized to potential where the highest intensity occurred for each cation, respectively.

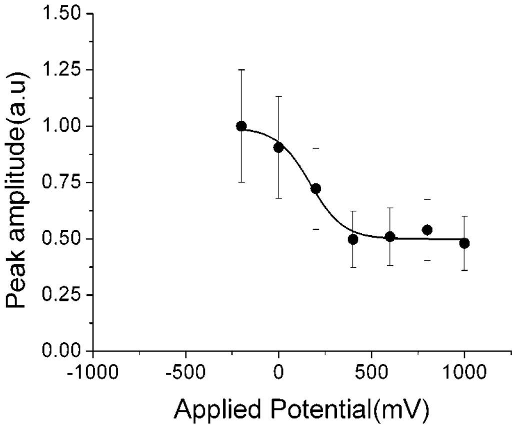

Figure 6. Potential dependence of D_2O peak for HSO_3CF_3 in 0.05× D_2O−acetonitrile solution. Potential scale is with respect to a Ag/AgCl reference.

The behavior of D_2O and acetonitrile is different in the presence of hydronium ion versus the alkali cationic solutions. The most notable effect is the limited potential window for the stability of H^+. The lower limit here is about −200 mV vs Ag/AgCl below which there is H_2 evolution from the Pt. Despite this, the low potential does appear to bring D_2O to the surface as a free hydronium, $(D)H^+D_2O$, ion. This lower frequency peak, red shifted ~150 cm^{-1}, is consistent with hydronium ion in water clusters.[20,21] The overall signal intensity is greater for the acid solution and the potential dependence, although shifted positive by 600 mV, is similar to that of the alkali cations (Figure 6). It is also notable that acetonitrile does not appear to "flip" orientation at more positive potentials as it does in alkali metal salt solutions. This is presumably due to the presence of protons that stabilize a side-bonded η^2-coordinated CN (CN parallel to the metal electrode) species as was observed by Weaver et al. in aqueous solution.[22]

The effect of potential on the acetonitrile molecules has been discussed thoroughly in a previous publication.[5] Briefly summarizing here, at potentials positive of 400 mV vs Ag/AgCl, acetonitrile is oriented with the CN group directed toward the metal (state I in Figure 4). As the potential becomes more negative, more acetonitrile molecules become oriented with the CH_3 pointing toward the metal (state II in Figure 4). This is explained as due to the surface charge causing the dipoles to reorient in response to the changing electric field. At the point where the number of molecules pointing up and down is equal, the surface charge is considered to be zero, which defines the potential of zero charge, or PZC. With no excess surface charge, the dipoles have no preferred orientation on the surface and the SFG signal goes to zero. This occurs near +400 mV vs Ag/AgCl.

In the bulk solution, the cations are solvated primarily by water, since this is the more polar component in the D_2O/CH_3CN solvent mixture. This is related to the commonly known salting out effect.[23,24] This may be viewed as cations with a primary solvation shell of water that are contained in the homogeneous solution of acetonitrile−water. For the concentrations used here, the bulk solutions are completely miscible.[17] However, it has been reported that the infrared spectra of miscible solutions also show significant broadening and frequency shifting (up to 100 cm^{-1} shifts) of the OD vibration with increasing water content. These effects are attributed to the formation of clusters between acetonitrile and water [12,17] even in miscible solutions. The presence of ions would further complicate this structure due to the combined effects of clustering and solvation.[23] These complications limit the degree of detail in the structure of the inner layer that be extracted from the vibrational spectra by themselves.

Despite the complexity in the vibrational spectra, there are clear changes of the D_2O peak with applied potential (Figure 5) that can be interpreted at least qualitatively. As the surface

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potential is adjusted more negatively, the cations will move from the outer diffuse double layer and into the Helmholtz layer.[25−27] When the cations move into the inner layer the solvent water molecules move with them to the surface. This is shown in Figure 5 for Li^+, K^+, Na^+, and Cs^+. In Figure 5, the potential where the D_2O signal starts to increase is dependent on the identity of the ion. The potential is most negative for Li^+ followed by K^+ then Na^+ and finally Cs^+. Water molecules are more tightly bound to the smaller cation as observed in thermodynamic and spectroscopic measurements.[28−33] The more tightly held the water molecules are the more work needs to be done to break the solvation shell, and this translates to the need for a more negative potential. The potential dependence of the OD vibrations observed here is interpreted to mean that as cations move to the inner Helmholtz layer the water of hydration becomes oriented with respect to the surface normal [34,35] and produces the signal that is detected with SFG (State III in Figure 4). The data for Cs^+ in Figure 5 would appear to be uniquely different from that of the other cations but in fact are not. The potential where the intensity of the OD symmetric stretch is maximized is shifted positively by about 800−1000 mV relative to the other three cations. This is due to the very low solvation energy of the large Cs^+ ion, such that only a small negative surface charge results in formation of the oriented water layer (the PZC in this solvent is ca. +400 mV vs Ag/AgCl [5]).

A summary of the potential dependence of the amplitude in both the OD and CH regions is given in Figure 7 for the Na^+ electrolyte. The potential dependence of these intensities can be accounted for in the model of Figure 4 and the effect of surface charge on the composition of the inner Helmholtz layer. Acetonitrile dominates the inner layer with the CN group directed toward the metal at potentials where the metal has a positive charge, at +400 to1200 mV vs Ag/AgCl. As the surface becomes negatively charged (at −200 to +400 mV), the acetonitrile orientation flips 180°, with the CH_3 group predominantly pointing toward the surface. At even more negatively charged surfaces, D_2O begins to displace acetonitrile from the surface and is the predominant molecule on the surface (at −200 to −800 mV). The potential where water is the dominant molecule at the surface is determined by the solvation energy of the cation, i.e., the more strongly solvated the cation the lower the potential for oriented water to form at the surface.

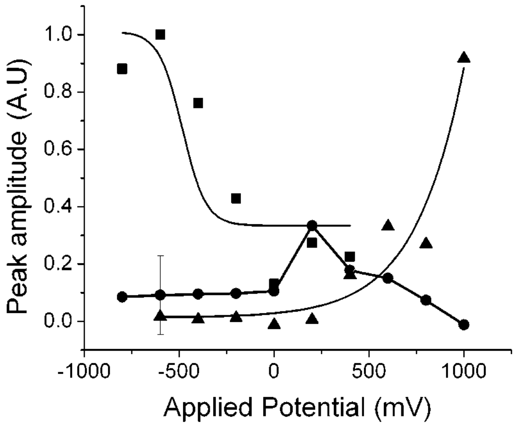

Figure 7. Scaled peak amplitude for different functional groups at fixed potentials: (■) ν_1 of D_2O, (▲) symmetric stretch of CH_3 in acetonitrile directed away from the surface, and (●) symmetric stretch of CH_3 in acetonitrile directed toward the surface. The electrolyte is 0.1 M $NaSO_3CF_3$. The potential is with respect to a Ag/AgCl reference. The curves are a guide for the eye.

Summary

Sum frequency generation allows the study of the vibrational spectra from molecules adsorbed at the metal/solution interface without contributions from the same molecules in the bulk solution. The results provide a very specific model for the composition of the inner Helmholtz layer as a function of potential and surface charge. Acetonitrile dominates the inner layer with the CN group directed toward the metal at potentials where the metal has a positive charge. As the surface becomes negatively charged, the acetonitrile orientation flips 180°, with its CH_3 group predominantly pointing toward the surface. At even more negatively charged surfaces, D_2O displaces acetonitrile from the inner layer and is present as an oriented molecule with the oxygen end pointing toward the metal. The potential (and surface charge) where water is the dominant molecule at the surface is determined by the solvation energy of the cation, i.e., the more strongly bound the water is to the cation, the more negative the potential.

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