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Complete List of Authors:	Balzerowski, Patrick; Ruhr University Bochum, Physical Chemistry II Meister, Konrad; FOM Institute for Atomic and Molecular Physics - AMOLF Versluis, Jan; FOM Institute for Atomic and Molecular Physics - AMOLF Bakker, Huib; FOM Intitute for Atomic and Molecular Physics - AMOLF,

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Heterodyne-detected Sum Frequency Generation Spectroscopy of Polyacrylic Acid at the Air/Water-Interface

Patrick Balzerowski,[b] Konrad Meister,*[a] Jan Versluis,[a] Huib J. Bakker [a]

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The conformational and hydration behavior of polyacrylic acid (PAA) at the air/water interface is studied using heterodyne-detected vibrational sum frequency generation spectroscopy (HD-VSFG). The amount of adsorption at the water-air interface and the influence of PAA on the water structure at the interface are found to be highly dependent on the degree of ionization (acid dissociation) of the carboxylic acid groups. At a low degree of ionization PAA is surface active and remains in a dense packing arrangement with intrachain hydrogen bonds. The interfacial water molecules show a net orientation with their OH groups pointing to the surface. Ionization of the carboxylic acid groups leads to an increase of the negative charge and to a break-up of the intrachain hydrogen bonds. The increase in negative charge is accompanied by an increase of the VSFG signal of the interfacial water molecules, as a result of their enhanced orientation. At ionization degrees $\alpha > 0.203$ PAA loses its enhanced surface propensity and is well desolved in the bulk. Addition of NaCl to the solution is observed to lead to a recurrence of PAA at the interface.

1 Introduction

Polyelectrolytes (PEs) are an important class of polymers that are used in several technological applications spanning from absorbing materials in baby diapers to oil recovery or nanofabrics.[1,2] In addition, PEs are often used as models for biomolecular systems due to their resemblance with biopolymers such as proteins or DNA.[3] All PEs contain ionizable groups that can be charged in aqueous solution. Depending on their functional group, PEs are denoted as anionic or cationic and classified further as strong or weak electrolytes. The material properties of PEs are highly dependent on the conformation of the polymer chains in solution, which in turn are determined by the electrostatic intermolecular interactions between the polymer chains, counter ions and the surrounding water.[4]

Polyacrylic acid (PAA) is a simple, relatively common anionic polyelectrolyte that consists of a hydrocarbon backbone to which carboxylic acid groups are bonded on alternate carbons, as illustrated in the inset of figure 1. Due to its carboxylate repetition unit PAA is often used as a model for more complex organic macromolecules that contain carboxylate functional groups such as humic acid compounds or proteins.[5] PAA is a weak polyacid for which the degree of ionization strongly depends on the pH. The degree of ionization strongly affects the properties of PAA in aqueous solution.[4,6,7] The resulting changes of the properties of PAA are mostly interpreted in terms of the conformational changes of the polymer and the associated structural changes of the hydration water.[6,8] Nevertheless, despite significant experimental and theoretical efforts, the details of the interactions between PAA, ions and water are not well understood.[9] Even less information is available for the properties of PAA at the water-air interface as only few experimental techniques are capable of directly probing this important and omnipresent interface. Surface tension studies showed that the adsorption behavior of PAA is strongly pH-dependent, but failed to provide molecular level information on the surface composition or hydration behavior.[10]

Richmond and coworkers proved that the properties of PAA and the interaction of PAA with ions can be readily investigated using conventional vibrational sum frequency generation spectroscopy (VSFG).[5,11] Here we investigate PAA at the air/water interface using heterodyne-detected vibrational sum frequency generation spectroscopy (HD-SFG). Unlike conventional VSFG that measures the absolute square of the second-order nonlinear susceptibility $\chi^{(2)}$, heterodyne-detected VSFG provides the imaginary (Im) and real (Re) parts of $\chi^{(2)}$ as a function of frequency. The sign of the Im[$\chi^{(2)}$] spectrum is directly connected to the absolute orientation of the molecules at the interface and therefore provides direct

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[a] FOM-Institute for Atomic and Molecular Physics AMOLF, Science Park 104, 1098XG Amsterdam, The Netherlands
[b] Physical Chemistry II, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany
* Corresponding author, E-mail: K.Meister@amolf.nl

information on the molecular-scale structure.[12] HD-SFG has been successfully used to investigate the structure and orientation of interfacial water at various interfaces, including lipids, proteins, polymers and polyelectrolytes.[9,13–15] Using this technique we are able to provide a complete molecular picture of the surface affinity and structure of PAA at the air-water interface in dependence of the degree of ionization and the ionic strength of the solution.

2 Experimental Section

2.1 Heterodyne-detected Sum Frequency Generation

The laser source of the VSFG setup is a regenerative Ti:Sapphire amplifier (Coherent) producing 800 nm pulses at a 1 kHz repetition rate with a pulse duration of 35 fs and a pulse energy of 3.2 mJ. Approximately two thirds of the laser output power are used to pump a home-built optical parametric amplifier and a difference-frequency mixing stage. This nonlinear optical device produces tunable broadband mid-IR pulses (ranging from $2-10\,\mu\mathrm{m}$, $600\,\mathrm{cm}^{-1}$ bandwidth at FWHM, $10-20\,\mu\mathrm{J}$). The IR pulses have a sufficiently large bandwidth to measure the complete VSFG spectrum of the OH stretch vibrations of H_2O. Another part of the 800 nm pulse is sent through a pulse shaper to narrow down its bandwidth to $\approx 15\,\mathrm{cm}^{-1}$. The resulting narrowband 800 nm pulse (VIS) and the broadband IR pulse are directed to the sample surface at angles of $\approx 41.5^\circ$ and $\approx 45.7^\circ$, respectively, to generate light at the sum frequency. The VIS and IR beams are focused in spatial and temporal overlap on the sample surface. The VSFG light generated at the surface is detected via a spectrograph (Spectrometer: Acton SP2356, Camera: Pixus 100B, both from Princeton Instruments). In heterodyne-detected VSFG the generated sum-frequency electric field is combined with a local oscillator (LO) electric field at the same frequency. The LO sum-frequency light is created by focussing the IR and VIS beam on a metal surface where a strong SFG signal is generated as a result of the strong non-resonant $\chi^{(2)}$ of the metal. The LO SFG signal is sent through a silica plate (≈1 mm) to introduce a small temporal delay with respect to the VIS and IR beams. The remaining IR and VIS beams are refocused on the sample interface to generate the VSFG signal of the sample. Both the LO SFG and the sample VSFG beams are collinear and coupled into the spectrograph. From the interference pattern the imaginary and real components of the frequency-dependent second-order susceptibility $\chi^{(2)}$ are extracted. To this purpose the detected interference pattern is Fourier transformed to the time domain. Afterwards only the time-delayed component representing the interference between the LO SFG and the sample VSFG is transformed back to the frequency domain. All HD-VSFG spectra in this paper were recorded with s-polarised SFG, s-polarised VIS, and p-polarized IR. The spectra are normalized to a reference SFG spectrum measured from z-cut quartz. The absolute phase of the VSFG signal is determined by comparing the heterodyne detected VSFG signal from the sample with the heterodyne detected VSFG signal from a reference z-cut quartz crystal. In this determination it is crucial that the reference z-cut quartz crystal is placed at the same height as the sample since a difference in height would result in a phase shift in the recorded spectra and the extracted $\chi^{(2)}$. This position is controlled by monitoring the VSFG signal on the CCD camera, which enables a determination of the height with an accuracy of $20\,\mu\mathrm{m}$.

2.2 Sample preparation and calculation of degree of ionization α

Polyacrylic acid was purchased from Sigma-Aldrich ($M_v \approx 450000\,\mathrm{g/mol}$) and was used without further purification. The HD-VSFG measurements were performed in ultrapure water (resistivity $> 18.2\,\mathrm{M\Omega cm}$). For the measurements in section 3.2 and the measurements represented by figure 3b) and c) in section 3.3 the pH was adjusted using sodium hydroxide. For all measurements the solutions were freshly prepared and spectroscopic measurements were conducted approximately 2 h after preparation at room temperature. The pH values of all solutions were checked before and after the HD-SFG measurements (Mettler Toledo FE20), enabling an accurate calculation of the degree of ionization of the PAA solutions. We put 5 ml of the sample solution in a sample reservoir made of teflon. After purging the sample compartment with nitrogen for 3 min, HD-VSFG spectra with an integration time of 220 s per sample were recorded. Measurements with an integration time of 30 s before and after recording the spectra showed no indication of any spectral changes. To ensure reproducibility, we performed all reported measurement series at least two times.

PAA belongs to the class of weak polyacids, thus the degree of ionization is strongly dependent on pH. In the case of a weak acid containing one acidic proton, the degree of ionization can be directly calculated from the acid dissociation constant pK_a. Because in polyacids dissociation of a single acidic group is always affected by the dissociation state of the remaining acidic groups on the polymer chain, the titration behaviour is better described by an extended version of the Henderson-Hasselbach equation.[16]

$$\alpha = \frac{10^{-\frac{pK_{a,app}}{n}}}{10^{-\frac{pH}{n}} + 10^{-\frac{pK_{a,app}}{n}}} \qquad (1)$$

Within this formalism the pK_a value is replaced by an apparent acid dissociation constant $pK_{a,app}$ and a constant n is introduced, which accounts for the cooperative nature of the dissociation. For the calculation of the degree of ionization we used values of $pK_{a,app} = 6.45$ and $n = 2.774$ at 0 mmol/L ionic strength and $pK_{a,app} = 5.4$ and $n = 2.5$ at 500 mmol/L.[17]

3 Results and Discussion

Figure 1a presents HD-VSFG spectra of water and an aqueous solution of PAA at the air/water interface measured in SSP polarization configuration (s-SFG, s-VIS, p-IR). The Im$[\chi^{(2)}]$ spectrum of the pure water/air interface shows a weak positive band between $2930\,\mathrm{cm}^{-1}$ and $3130\,\mathrm{cm}^{-1}$ and a stronger negative band between $3200\,\mathrm{cm}^{-1}$ and $3500\,\mathrm{cm}^{-1}$. The sign of the Im$[\chi^{(2)}]$ spectrum of the symmetric stretch vibration of water is directly related to the projection of the vibrational transition dipole moment onto the surface normal.[18] A positive sign of Im$[\chi^{(2)}]$ of the OH stretch vibrations corresponds to a net orientation of OH groups to the air while a negative sign of Im$[\chi^{(2)}]$ corresponds to OH groups point-

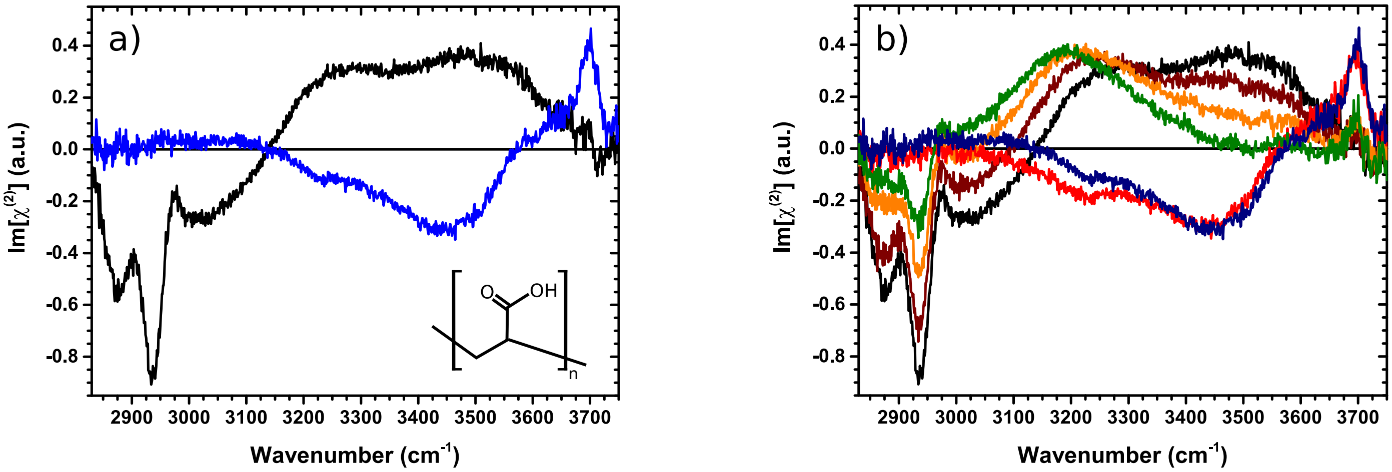

Fig. 1 (a) Imaginary $\chi^{(2)}$ spectra of water [blue] and PAA ($4.5\,\mathrm{g/L}$ (pH 2.8)) [black] at the air-water interface, measured in ssp polarization (s-SFG, s-VIS, p-IR). Inset shows the schematic structure of PAA. (b) Concentration dependent Imaginary $\chi^{(2)}$ spectra of aqueous PAA solutions: $4.5\,\mathrm{g/L}$ (black), $2.25\,\mathrm{g/L}$ (brown), $0.45\,\mathrm{g/L}$ (yellow), $0.225\,\mathrm{g/L}$ (green), $0.045\,\mathrm{g/L}$ (red) and pure water (blue).

ing into the liquid. At $3700\,\mathrm{cm^{-1}}$ the Im[$\chi^{(2)}$] spectrum shows a narrow band that can be assigned to free OH groups sticking out of the water surface. The Im[$\chi^{(2)}$] spectrum of the pure water/air interface of figure 1a) is in excellent agreement with the results of previous studies.[19–21]

In figure 1a) we also present the Im[$\chi^{(2)}$] spectra of an aqueous solution of PAA with a concentration of $4.5\,\mathrm{g/L}$ (pH 2.8). This spectrum strongly differs from the Im[$\chi^{(2)}$] spectrum of pure water. The Im[$\chi^{(2)}$] spectrum of the PAA solution shows narrow peaks in the frequency region $2800-3000\,\mathrm{cm^{-1}}$ associated with the CH vibrations of PAA. As a result of the long chain length of the studied PAA, the CH region contains only contributions from methylene (CH_2) groups and methine (CH) groups. The methylene group contributes a symmetric and asymmetric stretch vibration and a Fermi-Resonance, exhibiting identical symmetry as the symmetric stretch vibration. Together with the methine group this leads to four possibly visible resonances in the HD-VSFG spectra. In our spectra we can identify three resonances. Two negative bands appear at $\approx 2875\,\mathrm{cm^{-1}}$ and $\approx 2935\,\mathrm{cm^{-1}}$ and a weaker positive band is observed at $\approx 2975\,\mathrm{cm^{-1}}$. The presence of three resonances in the CH region at these frequencies is in agreement with previous IR and Raman studies of PAA[22] and previous SFG work of partially hydrated polyacrylamide.[9] In line with these previous studies we assign the negative bands at $\approx 2875\,\mathrm{cm^{-1}}$ and $\approx 2935\,\mathrm{cm^{-1}}$ to the stretch vibration of the methine group (ν_{CH}) and the symmetric stretch of the methylene group ($\nu_{CH_2,SS}$), respectively, and the positive band at $\approx 2975\,\mathrm{cm^{-1}}$ to the asymmetric stretch of the methylene group ($\nu_{CH_2,AS}$). This assignment of the bands in the CH region differs from the assignment of previous homodyne VSFG work on PAA.[5] In this previous work the modes at $2852\,\mathrm{cm^{-1}}$ and $2933\,\mathrm{cm^{-1}}$ were assigned to the symmetric and asymmetric CH_2 stretch vibration which led them conclude that the backbone of PAA must be aligned along the surface plane. However, the present heterodyne-detected VSFG spectra reveal that this assignment cannot be correct due to the identical sign of these modes in the Im[$\chi^{(2)}$] spectrum. We hope that the present results will stimulate computational efforts that can corroborate and/or refine the assignment of the CH bands.[23,24]

Based on the negative sign of the $\nu_{CH_2,SS}$ and the positive sign of the $\nu_{CH_2,AS}$ we can deduce that the methylene groups have a net orientation with the CH bonds pointing towards the interface.[20,25] The negative sign of the ν_{CH} band indicates that the methine groups is also pointing preferentially towards the surface. This finding shows that both the CH and CH_2 groups have a net orientation towards the air phase, meaning that the carboxylic acid groups will be more strongly embedded in the bulk of the solution. This result is in line with the fact that the carboxylic acid group is the most hydrophilic group of PAA.

We observe additional PAA specific signals at $\approx 3050\,\mathrm{cm^{-1}}$ and $\approx 3580\,\mathrm{cm^{-1}}$. The infrared spectra of carboxylic acids also show a band around $3050\,\mathrm{cm^{-1}}$ that is assigned to cyclic carboxylic-acid dimers.[26] Hence, we assign the band at $\approx 3050\,\mathrm{cm^{-1}}$ to a similar resonance of carboxylic acid dimers resulting from inter- or intrachain double hydrogen bonds of the PAA chains, thus forming temporal cross-links.[27] In bulk solution uncharged polyelectrolytes adopt a random coil conformation similar to polymers without ionizable groups. Since PAA provides the possibility to form intramolecular hydrogen bonds under acidic conditions, as apparent from the signal at $3050\,\mathrm{cm^{-1}}$, this random coil conformation will be even enhanced. Considering these facts and the assignment in the CH stretch region we conclude that PAA molecules remain mostly in a compact random coil conformation at the interface and only some partially ordered subunits align along the interface with methylene and methine groups both pointing towards the interface.

The band at $\approx 3580\,\mathrm{cm^{-1}}$ is assigned to a carboxylic acid group that is hydrogen bonded to surface water molecules. It is most likely that this resonance originates from the dangling OH of the carboxylic acid group of which the carbonyl moiety acts as a hydrogen-bond acceptor for interfacial water molecules. This assignment agrees with previous assignments of the resonance observed for the carboxylic acid headgroups of lipids at the air-water interface.[28,29]

Figure 1b) shows the Im[$\chi^{(2)}$] spectra of aqueous PAA solutions with concentrations ranging from 0.045 g/L ($\alpha \approx 0.146$) to 4.5 g/L ($\alpha \approx 0.050$). The observed changes in the spectra are not the result of a change of the degree of ionization α, as α remains below < 0.2. In figure 2 it is shown that these low ionization values do not lead to a strong change of the spectral shape. At the lowest concentration of 0.045 g/L the PAA spectrum resembles that of pure water, showing a negative band at $\approx 3200-3450\,\mathrm{cm}^{-1}$ and the positive dangling OH contribution at $\approx 3700\,\mathrm{cm}^{-1}$. When the concentration of PAA is increased to 0.225 g/L, the spectrum changes considerably. The negative feature at $\approx 3200-3450\,\mathrm{cm}^{-1}$ vanishes and is replaced by a broad positive band at $\approx 3200\,\mathrm{cm}^{-1}$. This observation can either be explained by sufficiently slightly negatively charged PAA present at the interface already at low bulk PAA concentrations or by a stronger hydrogen bonding between water and undissociated carbonyl groups. In both scenarios water molecules will be flipped to a net orientation with the hydrogen atoms pointing towards the surface. In addition, the intensity of the dangling OH peak decreases and CH stretch vibrational signals at $\approx 2875\,\mathrm{cm}^{-1}$,$\approx 2935\,\mathrm{cm}^{-1}$ and $\approx 2975\,\mathrm{cm}^{-1}$ appear. At concentrations of 2.25 g/L and 4.5 g/L the broad negative band at $\approx 3050\,\mathrm{cm}^{-1}$ associated with inter- or intrachain hydrogen bonds becomes clearly visible. With the rise of this (negative) band and the rise of the additional positive PAA specific band at $\approx 3580\,\mathrm{cm}^{-1}$ the VSFG spectrum shows a strong blue-shift. At the highest concentrations of 2.25 g/L and 4.5 g/L the PAA specific contributions dominate and the interfacial water contributions are less apparent. This behavior is consistent with surface tension data, which show a steady decrease of the surface tension with increasing concentration at concentrations larger than ≈ 0.225 g/L.

3.1 Changing the Degree of Ionization of Polyacrylic Acid

The pK_a value of PAA has been reported to be ≈ 6.45 and thus PAA belongs to the class of weak polyelectrolytes.[17] With the pK_a value we can calculate the degree of ionization as described in the experimental section. The structure of polyelectrolytes in aqueous solution is highly dependent on the degree of ionization. An increase of the pH leads to deprotonation of the carboxylic acid groups and thus to an increase of the negative charge density on PAA. The additional long range electrostatic interactions along the polymer backbone lead to structural changes of the polyelectrolyte. An interesting question is how the changes in charge and structure of PAA influence the water network at the air/water interface. To investigate this we measured HD-VSFG spectra at different pH values.

Figure 2 shows HD-VSFG spectra of a 4.5 g/L PAA solution at different pH and corresponding different degrees of ionization α. Increasing the pH from 2.8 ($\alpha \approx 0.046$) to 4.2 ($\alpha \approx 0.134$) yields only minor changes. This increase in pH leads to a slight decrease of the negative signals in the CH region and a small increase of the broad water band at $\approx 3200\,\mathrm{cm}^{-1}$. A further increase of the pH to 4.8 ($\alpha \approx 0.203$) leads to several effects in the Im[$\chi^{(2)}$] spectrum. All signals in the CH region decrease and the band at $\approx 3050\,\mathrm{cm}^{-1}$ clearly starts to lose intensity, as a result of the deprotonation of the carboxylic acid group. The most pronounced change is observed for the broad water band at $\approx 3200\,\mathrm{cm}^{-1}$ that reaches a maximum at pH 4.8 ($\alpha \approx 0.203$). Since the CH signals do not increase in intensity going from pH 4.2 to 4.8 the increase of the $\approx 3200\,\mathrm{cm}^{-1}$ band is unlikely the result of an increase of the surface concentration of PAA. Hence, the increase of the water band at $\approx 3200\,\mathrm{cm}^{-1}$ likely results from the increased number of ionized carboxyl groups along the PAA molecules. These negatively charged groups enhance the orientation of the water molecules with their OH group to the negatively charged PAA at the surface. The water orientation can be further enhanced by a partial uncoiling of the PAA molecules. Both experiment and theory show that in bulk solution the persistence length of polyacrylic acid increases upon ionization of the carboxylic acid group due to the associated increase of the electrostatic repulsion.[8,30,31] This uncoiling is consistent with the significant decrease of the carboxylic acid dimer specific band around $\approx 3050\,\mathrm{cm}^{-1}$.

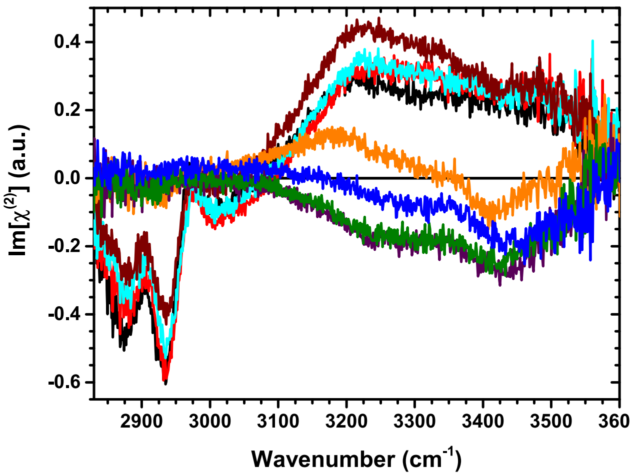

Fig. 2 Imaginary $\chi^{(2)}$ spectra of aqueous PAA at different pH and corresponding different degrees of ionization α: $pH = 2.8$ ($\alpha \approx 0.046$) [black], $pH = 3.3$ ($\alpha \approx 0.068$) [red], $pH = 4.2$ ($\alpha \approx 0.134$) [cyan], $pH = 4.8$ ($\alpha \approx 0.203$) [brown], $pH = 5.3$ ($\alpha \approx 0.278$) [orange], $pH = 6.1$ ($\alpha \approx 0.428$) [purple], $pH = 12.6$ ($\alpha \approx 1$) [green] and water [blue].

As the pH is further raised to 5.3 ($\alpha \approx 0.278$) a dramatic change in the Im[$\chi^{(2)}$] spectrum is observed and all specific PAA signals completely vanish and the broad water band at $\approx 3200\,\mathrm{cm}^{-1}$ strongly decreases leaving only a weak positive band, indicating that part of the previously observed orientation of interfacial water molecules remains. In addition, a weak negative band at $\approx 3400\,\mathrm{cm}^{-1}$ arises, suggesting the formation of a hydrogen bond network at the interface comparable to pure water.

Raising the pH to 6.1 ($\alpha \approx 0.428$) results in a spectrum that has only negative contributions and that resembles the spectrum of pure water in the region from $\approx 3200-3500\,\mathrm{cm}^{-1}$. The observed behavior for pH values greater than 5.3 ($\alpha \approx 0.278$) can be well explained from a charge density dependent surface propensity of PAA. Apparently at a degree of ionization of ≈ 0.278, the solvation of PAA in the bulk becomes highly favorable, and thus the concentration of PAA at the surface is no longer enhanced.

3.2 Effect of Ionic Strength

The conformation of polyelectrolytes is governed by electrostatic interactions along the polymer chain and between the polymer and the solution. In aqueous solutions the latter interactions strongly depend on the presence of free ions. As a result an increase of the ionic strength generated by free ions can effect the degree of ionization of polyelectrolytes. Hence, variation of the ionic strength often induces conformational changes due to altered electrostatic inteactions. We investigate the influence of ionic strength on PAA at different degrees of ionization by adding different amounts of sodium chloride (NaCl) to the solution.

Figure 3 shows the effect of adding up to 500 mmol/L sodium chloride to PAA solutions of 4.5 g/L starting at various degrees of α ($\alpha \approx 0.051$, ≈ 0.527, ≈ 0.916). Using equation(1) an estimation of the increase in the degree of ionization for the highest concentration of NaCl in our experiments can be calculated. For the measurement series starting at $\alpha \approx 0.051$ an increase up to ≈ 0.072 for the maximum concentration of 500 mmol/L NaCl is expected. In our measurements at low α (Figure 3a) the addition of sodium chloride and hence the increase of ionic strength of the solution leads to a decrease and eventual sign change in the $\approx 3200-3300\,\mathrm{cm}^{-1}$ region. No other structural changes or any indications of a depletion of PAA from the interface in the presence of sodium ions are observed, as evident by the unchanged response in the CH region of the spectrum.

The region from $\approx 3200-3300\,\mathrm{cm}^{-1}$ is attributed to water molecules participating in strong hydrogen bonds. As the degree of ionization is expected to be still low even at an ionic strength of 500 mmol/L the decrease of the response in this region can most likely be explained by a screening effect caused by the added salt ions. With increasing salt concentration the negative charge at the interface associated with ionized PAA carboxylic acid groups gets screened by sodium ions, thus reducing the orientation effect on the interfacial water molecules.

In the measurement series at higher degrees of ionization ($\alpha \approx 0.527$, $\alpha \approx 0.916$) PAA shows very little surface propensity, thus yielding a VSFG spectrum that resembles that of pure water. However, at $\alpha \approx 0.527$ we clearly observe a recurrence of PAA to the interface for NaCl concentrations > 100 mmol/L. The spectra for solutions containing 300 mmol/L and 500 mmol/L NaCl show a broad positive band between 3100 and 3600 cm^{-1} showing the presence of negatively charged PAA at the interface. Based on equation(1) for an ionic strength of 500 mmol/L a change of α to 0.495 can be expected for the PAA solution with an initial α of 0.527 (figure 3b). As seen from figure 2 a recurrence to the surface is unexpected for such a degree of ionization. Apparently, the screening of the charges of PAA in the bulk by the salt ions reduces the solubility of PAA in the bulk, making it accumulate at the interface. This observation constitutes a salting out of the partially ionized PAA from its bulk solvation state. At $\alpha \approx 0.5$ PAA contains many negatively charged carboxylate groups, which act as acceptors of hydrogen bonds from water molecules. These water molecules have their OH pointing to the interface thus explaining the strong positive signal in the $\mathrm{Im}[\chi^{(2)}]$ spectrum. The spectrum extends quite far to low frequencies because these hy-

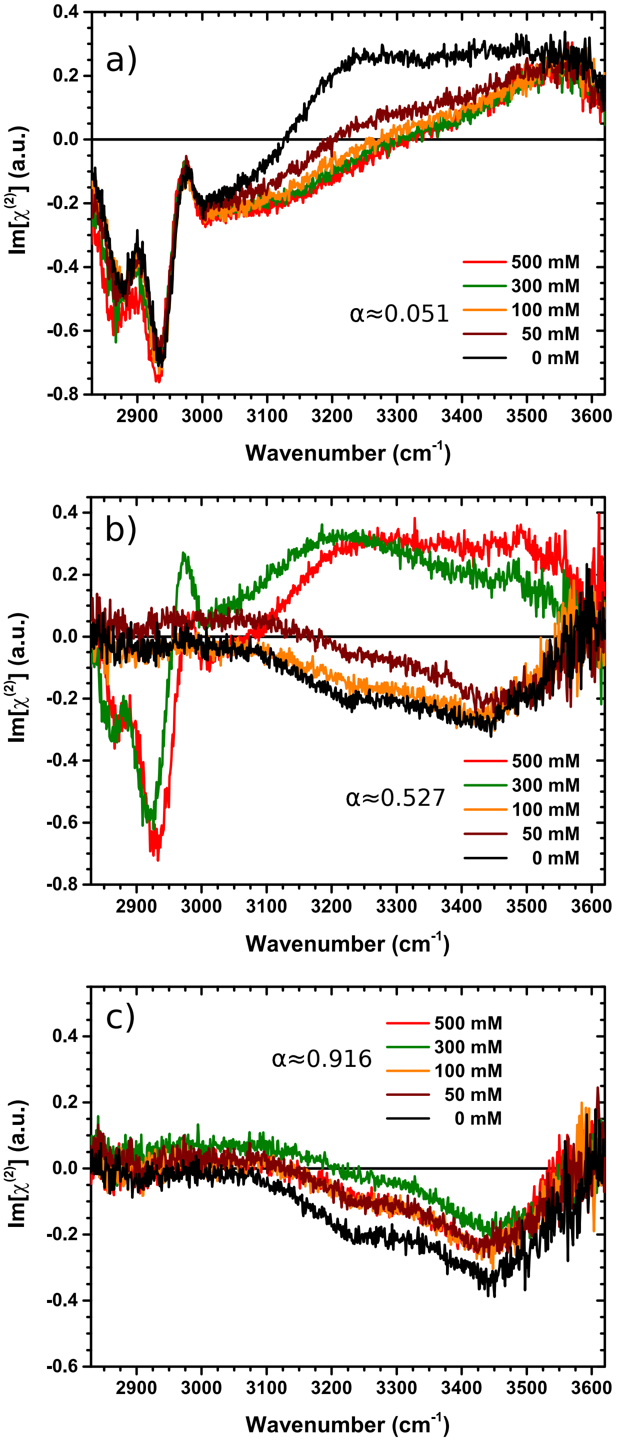

Fig. 3 Spectra of PAA (4.5 g/L) with different NaCl concentrations added: 0 mM NaCl (black), 50 mM NaCl (brown), 100 mM NaCl (yellow), 300 mM NaCl (green), 500 mM NaCl (red). The values for α are calculated via equation(1) and correspond to the solutions with 0 mM NaCl.

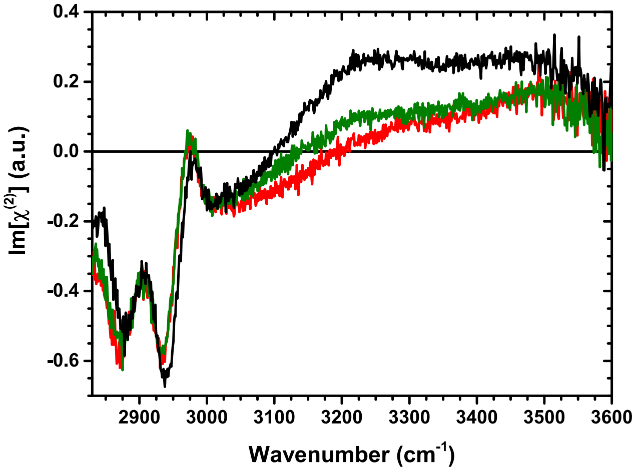

Fig. 4 Spectra of PAA (4.5 g/L) at $\alpha \approx 0.051$ (black) and with 50 mM NaCl (green), 50 mM CsCl (red) added.

drogen bonds can be quite strong.

As shown in figure 3c) in the measurement series with PAA starting at $\alpha \approx 0.916$ no recurrence is observed and all the spectra look comparable to the spectrum of pure water. From equation(1) we calculate the degree of ionization for the solution with the maximum concentration of NaCl to be ≈ 0.910. These results indicate that the amount of added sodium ions is not sufficient to lower the net charge of the ionized PAA to a level at which a salting out from its solvation state in the bulk can take place.

The salting-out effect can be strongly dependendent on the type of salt added.[32,33] Figure 4 illustrates that the addition of CsCl leads to smaller values of Im[$\chi^{(2)}$] in the region $3200 - 3300\,\mathrm{cm}^{-1}$. This result shows that Cs^+ ions are more effective in shielding the negative charges of PAA than Na^+ ions. In terms of the HSAB concept (*H*ard and *S*oft *A*cids and *B*ases, Pearson concept) this is unexpected, since the harder sodium ions should preferably be able to form stronger ion pairs with the carboxylate groups. The observed effect can probably be explained from a difference in interfacial salt concentration. Ions with a bigger ionic radius and higher polarizability (softer ions in terms of the HSAB concept) have a higher surface propensity compared to smaller less polarizable ions. Hence, for the same bulk salt concentrations of CsCl and NaCl, the interfacial concentration of Cs^+ is higher than the interfacial concentration of Na^+, thus yielding a more effective screening of the negative charges of PAA.

4 Conclusions

We study the properties of the surface of solutions of polyacrylic acid (PAA) in water using heterodyne-detected vibrational sum-frequency generation spectroscopy (HD-VSFG). With this technique we determine the real and imaginary parts of the second-order susceptibility $\chi^{(2)}$. The sign of Im[$\chi^{(2)}$] at a particular frequency is directly related to the orientation of the molecular group showing a vibration at that frequency. Already at low concentrations of PAA (> 0.045 g/L), we observe that the overall negative Im[$\chi^{(2)}$] spectrum of pure water (indicating a net orientation of water OH groups to the bulk) changes into a positive Im[$\chi^{(2)}$] spectrum, indicating a flipping of the net water orientation. This result shows that PAA has a high surface propensity. We vary the degree of ionization (acid dissociation) of PAA by varying the pH. We find that both the CH_2 (methylene) and CH (methine) groups of the polymer are oriented such that the CH bonds are pointing towards the interface. The Im[$\chi^{(2)}$] spectrum also shows a band at $3050\,\mathrm{cm}^{-1}$ indicating the formation of COOH dimers. From these responses we conclude that PAA remains in a dense random coil conformation at the air/water interface at low degrees of ionization.

We find that the amplitude of the positive Im[$\chi^{(2)}$] spectrum increases as the degree of ionization is increased with its maximum value at $\alpha \approx 0.203$. At higher degrees of ionization, the surface propensity of PAA decreases because of the increased negative charge of the polyelectrolyte. We also study the effect of ionic strength on the response of the surface of the PAA solutions. At low degrees of ionization ($\alpha \approx 0.051$), the addition of NaCl leads to a partial screening of the negative charges of PAA at the surface, leading to a decrease of the net orientation of the water molecules. This screening effect is found to be stronger for the addition of caesium chloride, which can be explained from the higher interfacial concentration of Cs^+ ions compared to Na^+ ions. At intermediate degrees of ionization ($\alpha \approx 0.527$), PAA has very little surface propensity, but this propensity can dramatically increase by adding NaCl to the solution. Apparently the screening of the negative charges of the carboxylate groups of PAA in the bulk by the Na^+ ions reduces the solubility of PAA, thus leading to an accumulation of PAA at the surface. This effect is highly reminisenct of a Hofmeister-like salting out of PAA from its solvation state in the bulk.

Our findings shed light on the behaviour of a common polyelectrolyte PAA at the air-water interface and provide molecular-scale information on the response of PAA to variations in macroscopic solution properties such as pH and ionic strength. Understanding the behaviour of such a simple polyelectrolyte might help to reveal the more complicated behaviour of biopolymers such as proteins or heterogeneous polymer mixtures.

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