

Molecular orientation of small carboxylates at the water-air interface

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Abstract: We study the properties of formate (HCOO^-) and acetate (CH_3COO^-) ions at the surface of water using heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy. For both ions we observe a response of the symmetric (ν_s) and antisymmetric (ν_{as}) vibrations of the carboxylate group. The spectra further show that for both formate and acetate the carboxylate group is oriented toward the bulk, with a higher degree of orientation for acetate than for formate. We find that increasing the formate and acetate bulk concentrations up to 4.5 m does not change the orientation of the formate and acetate ions at the surface and does not lead to saturation of the surface density of ions.

Carboxylic acid ($-\text{COOH}$) and carboxylate ($-\text{COO}^-$) groups are involved in many important interfacial processes, such as molecular recognition at bio-membranes, protein folding, and energy conversion and storage.¹⁻⁸ The chemical and physical properties of the carboxylate anion differ strongly from those of the conjugate carboxylic acid.⁹⁻¹¹ Further, carboxylates form strong ionic bonds with different metal cations, giving rise to metal carboxylates as well as more elaborate structures such as carboxylate based metal organic frameworks.¹²⁻¹⁶ Long-chain carboxylates are also frequently utilized as surfactants to solubilize hydrocarbons in fuel extraction.^{17,18} During the last decades, the pronounced surface activity of long-chain carboxylic acids and long-chain carboxylates inspired many studies of the acid/base equilibrium, the surface propensity, and the orientation properties of these systems in dependence on the chain length, the concentration and the pH.¹⁹⁻²³ Surface-specific X-ray photoelectron spectroscopy (XPS) studies showed that the surface propensity increases with increasing chain length.²⁴ Furthermore, it has been shown that the carboxylic acid has a higher surface affinity compared than its conjugate carboxylate anion.²⁴ While many studies have been devoted to the properties of long-chain carboxylic acids and carboxylates at aqueous surfaces, much less attention has been given to the surface properties of small carboxylate ions, as acetate and formate. Surface tension measurements and MD simulations indicate that the propensity of formate and acetate to be located at the surface of water strongly differ: while the addition of formate does not significantly change the surface tension, adding acetate does lead to a substantial lowering of the surface tension compared to water.^{25,26} In this work we perform HD-VSFG measurements to investigate the surface properties of aqueous sodium formate and sodium acetate solutions. For both formate and acetate, we observe a vibrational surface response of the carboxylate group, and we can establish the net orientation of these ions at the solution surface. We compare our results with the results of surface tension measurements and MD

simulations of the surfaces of aqueous solutions of formate and acetate.

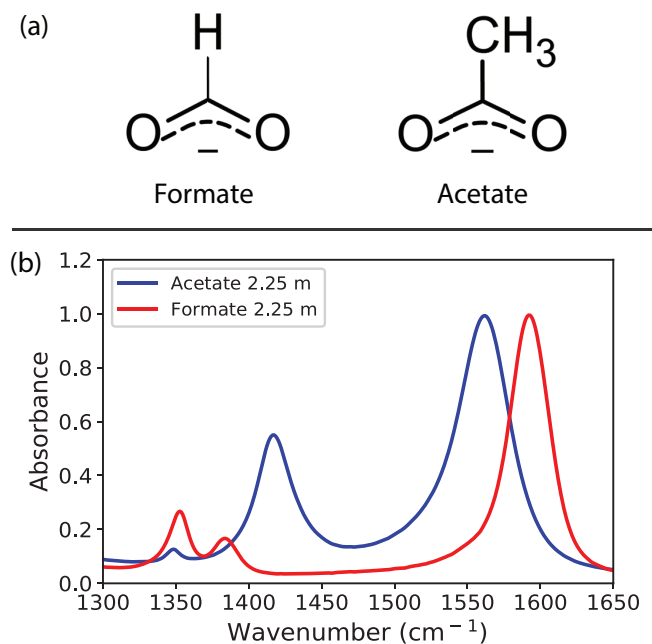


Figure 1. Normalized FTIR spectra of 2.25 m D_2O solutions of sodium formate (red) and sodium acetate (blue) in the frequency region of 1300 -1650 cm^{-1} .

We prepared 1-5 molal (m) solutions of formate and acetate in D_2O by mixing of D_2O with the appropriate amount of salt in a vial. We used sodium formate ($\geq 99.0\%$, Fluka Analytical), sodium acetate (anhydrous, for molecular biology $\geq 99\%$, Sigma Aldrich) and D_2O (99.9% atom D, Aldrich) as received.

The linear infrared absorption spectra were recorded with a commercial Bruker Vertex 80v Fourier-transform infrared spectrometer with a resolution of 2 cm^{-1} in transmission geometry. The samples were prepared by squeezing a droplet of the solution between a pair of circular 20 mm thick CaF_2 windows (Crystran) separated by a 5-25 μm thick PTFE spacer. The thickness of the spacers was adjusted such that the absorption of the carboxylate ions did not saturate. An empty cell with two identical CaF_2 windows was used for background measurements.

The technique of heterodyne-detected vibrational sum-frequency generation (HD-VSFG) was pioneered by Shen and coworkers in 2005 and ever since successfully used in a large number of surface studies.^{3,27,28} Here, we give a brief description of our implementation of HD-VSFG. A detailed description of the technique can be found in previous publications.²⁸⁻³¹ Our setup is based on a commercial amplified

Ti:sapphire laser source that delivers 80 fs pulses centered at 800 nm with an energy of 6.5 mJ and a repetition rate of 1 kHz. One part of these pulses is used to pump a commercial optical parametric amplifier (OPA, Light Conversion HE-TOPAS) that generates tunable infrared (ω_{IR}) (2.5 to 10 μm) pulses with a spectral bandwidth of 400 cm^{-1} . The other part of the 800 nm laser output (ω_{VIS}) is spectrally narrowed to a bandwidth of $\sim 20 \text{ cm}^{-1}$. The IR and 800 nm beams are spatially and temporally overlapped at the surface of a gold mirror to create a sum-frequency generation (SFG) signal (ω_{SFG}) ($\omega_{IR} + \omega_{IR} = \omega_{SFG}$), that serves as a local oscillator (LO-SFG). The incidence angles of the infrared (IR) and the 800 nm beam with respect to the surface normal are $\sim 55^\circ$ and $\sim 50^\circ$, respectively. The LO-SFG signal is sent through a silica plate with a thickness of $\sim 1 \text{ mm}$ to delay it in time ($\sim 1.6 \text{ ps}$) with respect to the IR and the 800 nm pulses. Subsequently, the 800 nm beam (s-polarized), the IR beam (p-polarized) and the LO-SFG signal (s-polarized) are focused on the sample surface, where the IR and the 800 nm beam generate a second SFG signal. The SFG signal of the sample and the LO-SFG signal are collinear and sent together into a spectrograph and detected with a thermoelectrically cooled charged-coupled device (CCD, Princeton Instruments). From the interference spectrum of the two SFG signals the real (Re) and the imaginary (Im) $\chi^{(2)}$ spectra can be extracted, providing direct information on the orientation of the vibrational transition dipole moments, and thereby on the orientation of the molecules at the surface.²⁹ The measured spectral response is corrected for the spectral dependence of the input IR beam by dividing the HD-VSFG spectrum of the sample by the HD-VSFG spectrum of a reference z-cut quartz crystal. In this normalization, it is important that the surface of the z-cut quartz crystal is at the same height as the sample, as a difference in height will lead to an error in the determination of the phase of the VSFG light and thus of the phase of $\chi^{(2)}(\omega)$. By monitoring the position of the VSFG-signal on the EMCCD, we can control the height of the reference z-cut quartz crystal to such an extent that the overall phase uncertainty is $\sim \pi/10(20^\circ)$. In the frequency region of 1300 - 1650 cm^{-1} an etalon effect occurs in the CCD camera. To correct the data for this effect we take two independent measurements of a z-cut quartz crystal with an orientation that differs by 180° . Thereby we obtain two reference spectra that differ in phase by 180° . By adding up these two reference spectra the interference of the SFG signal of the local oscillator and that of the quartz is removed. As a result, the remaining modulation purely represents the etalon effect, and this signal can now be used to correct the HD-VSFG spectrum of the sample for this effect. A more detailed explanation of this procedure can be found in the previous study.³² The typical acquisition time of a single HD-VSFG spectrum is 600 seconds.

In Figure 1, we show the normalized FTIR spectra of solutions of 2.25 m sodium formate and sodium acetate in D_2O in the 6 μm region. The high-frequency band is assigned to the antisymmetric stretch vibration (ν_{as}) of the carboxylate group. For formate this band is centered at 1590 cm^{-1} and for acetate at 1565 cm^{-1} . The low-frequency band is assigned to the symmetric stretch vibration (ν_s) of the carboxylate group and is centered at 1352 cm^{-1} for formate and at 1417 cm^{-1} for acetate. For the formate solution an additional band at 1380 cm^{-1} is observed which has been assigned earlier to the in-plane C-H bending vibration.³³ For acetate an additional band at 1350 cm^{-1} band is observed

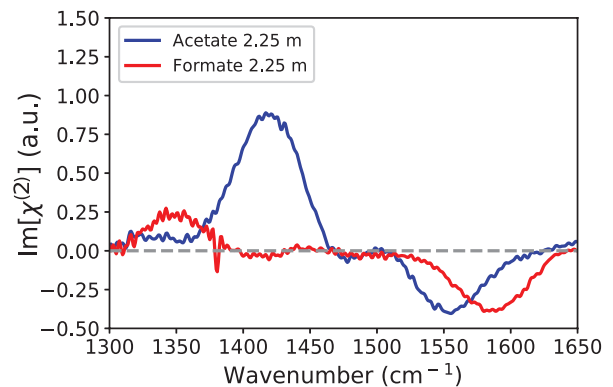


Figure 2. $\text{Im}[\chi^{(2)}]$ spectra of a solution of 2.25 m sodium formate (red) and sodium acetate (blue) in D_2O in the frequency region of 1300 -1650 cm^{-1} . The measurements are taken in SSP polarization configuration.

which can be assigned to the CH_3 deformation vibration. The symmetries of the CH vibrations and ν_s are different (A1 and B1 respectively) and hence mixing between these bands is formally not possible.³³⁻³⁶ To compare the absorption strengths of the different bands, we normalize the spectra on the maximum amplitudes of the ν_{as} vibrations. We observe that the ν_s vibration is almost twice as intense for acetate than for formate. We studied the concentration dependence of the bands (Figures 1 and 2 of the Supporting Information), and found that the ratio between the bending mode of D_2O ($\delta_{\text{D}_2\text{O}}$) and the ν_s of the carboxylate ions scales very well with the solute concentration. We also observe that both for formate and acetate the line shapes of the carboxylate stretch vibrations are quite independent of the concentration.

Figure 2 presents the imaginary part of the HD-VSFG spectra ($\text{Im}[\chi^{(2)}]$) of solutions of 2.25 m sodium formate (red) and sodium acetate (blue) in D_2O in the frequency region of 1300 - 1650 cm^{-1} . The $\text{Im}[\chi^{(2)}]$ spectra show a positive band at 1350 $\text{cm}^{-1}/1410 \text{ cm}^{-1}$, and a negative band at 1590 $\text{cm}^{-1}/1550 \text{ cm}^{-1}$ for formate/acetate. In line with the FTIR spectrum, we assign the low-frequency band to the ν_s vibration and the high-frequency band to the ν_{as} vibration of the carboxylate group. In SSP polarization combination only vibrational modes with a transition dipole moment (TD) component parallel to the surface normal can be observed. Hence, considering that the TD of the ν_{as} vibration of the carboxylate group is perpendicular to that of ν_s , only the latter vibration would have been detected in case the carboxylates would have their molecular c-axis parallel aligned with the surface normal. In earlier studies of long-chain carboxylates only the band of the ν_s vibration of the carboxylate group was observed in SSP polarization combination, indicating that for long-chain carboxylates the c-axis is indeed oriented parallel to the surface normal. For long-chain carboxylates the ν_{as} band could only be observed in SPS polarization configuration.^{22,23} Thus, the observation of the ν_{as} band in Figure 2 for formate and acetate shows that for these carboxylates the molecular c-axis is at a nonzero angle with respect to the surface normal. We observe that for both carboxylate solutions the ν_s vibrational mode has a positive sign in the $\text{Im}[\chi^{(2)}]$ spectrum. As the transition dipole mo-

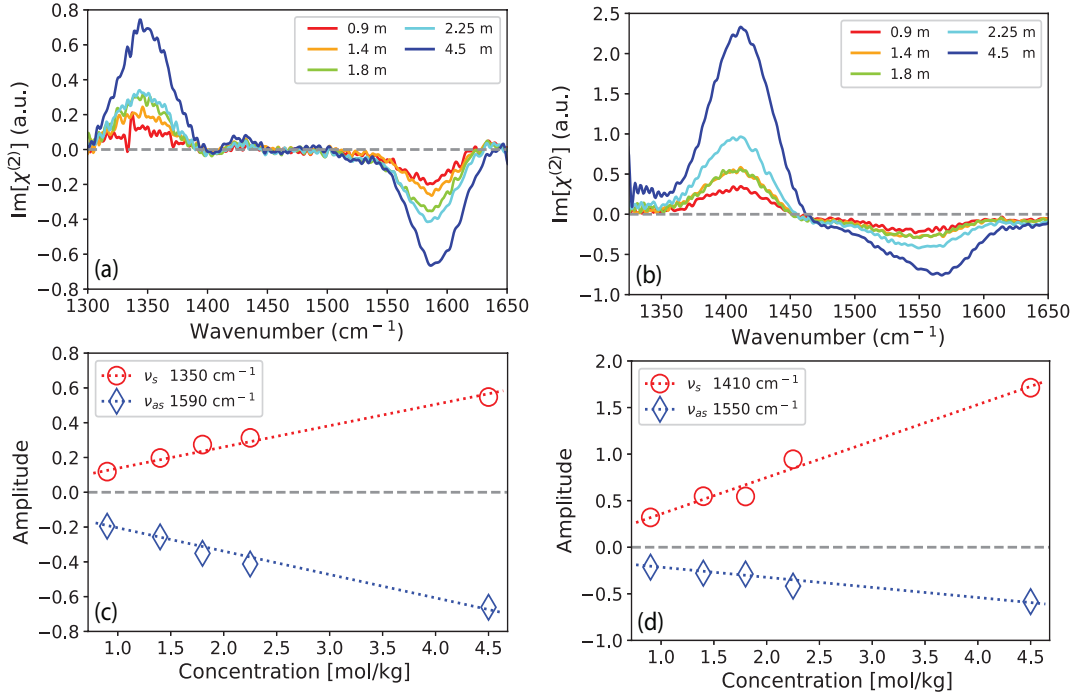


Figure 3. $\text{Im}[\chi^{(2)}]$ spectra of aqueous (a) sodium formate and (b) sodium acetate solutions in D_2O with different concentrations in the range of 0.9 - 4.5 m. ((c)-(d)) show the amplitudes of the bands of the ν_s and ν_{as} vibrations as a function of the carboxylate concentration.

ment of the ν_s vibration is aligned parallel to the c-axis of the carboxylate group, this observation implies that formate and acetate orient with their carboxylate group toward the bulk. HD-VSFG measurements of formate and acetate solutions performed in the $3 \mu\text{m}$ region support this assignment (Supporting Information, Figure 6), as these measurements show a negative sign of the C-H stretch vibration of the methine group of formate (ν_{CH}) and the symmetric CH_3 stretch vibration of the methyl group of acetate ($\nu_{\text{CH}_3,SS}$). These negative signs show that the C-H bonds of the carboxylate anions have a net orientation pointing toward the air.²⁸ Comparing figures 2 and 1, we note that in the SFG spectrum the ν_{as} band is substantially weaker compared to the ν_s band than in the FTIR spectrum. This difference can be explained from the fact that the $\chi^{(2)}$ response measured in HD-VSFG is proportional to the product of the TD and the Raman transition matrix element. The ν_{as} vibration shows only weak Raman activity compared to the ν_s vibration,³³ thus decreasing the SFG signal of the ν_{as} vibration relative to that of the ν_s vibration.

We observe in Figure 2 that the amplitudes of the ν_{as} bands of the sodium formate and sodium acetate solutions are almost the same. In previous surface-specific studies it was found that acetate has a quite high surface propensity, while formate was found to have a very low surface propensity.^{24,26} In view of this difference in surface propensity, it is quite unexpected that the VSFG response of ν_{as} is about equal in amplitude for acetate and formate solutions. The effect of the higher surface propensity of acetate is probably compensated by a larger tilt angle of the c-axis with respect to the surface normal for formate. A larger tilt angle enhances the amplitude of the band of the ν_{as} vibration. To further investigate this interpretation, we also performed

HD-VSFG measurements of acetate and formate solutions in SPS polarization combination that we compare to measurements in SSP polarization combination. In Figure 8 of the Supporting Information we show $\text{Im}[\chi^{(2)}]$ of 2.5 m sodium acetate and 4.5 m sodium formate solutions in D_2O measured in SPS polarization combination and we compare the results with the spectra measured in SSP polarization combination. From the combined data, we obtain for acetate a tilt angle θ of 45° and for formate significantly larger than 45° but smaller than 90° . In Figure 9 of the Supplementary Information we show that the value of the tilt angle of 45° of acetate is quite robust with respect to the width of the angular distribution. In Figure 3 we show $\text{Im}[\chi^{(2)}]$ spectra of (a) sodium formate and (b) sodium acetate solutions at different concentrations in the range of 0.9 - 4.5 m. In Figure 3 (c,d) we show the amplitudes of the two vibrational modes as a function of the carboxylate concentration for formate and acetate. For both formate and acetate, we observe that the amplitudes of the ν_s and ν_{as} bands increase linearly with the bulk concentration. This result shows that the surface does not get saturated with formate/acetate ions up to bulk concentrations of 4.5 m. Sodium acetate and sodium formate are relatively small molecular ions and show a significantly lower surface propensity compared to surfactants like stearate that have long hydrophobic tails. Hence, the effect of surface adsorption becomes visible only at relatively high salt bulk concentration (> 1 m). Another consequence of the limited surface propensity is that the surface coverage does not saturate, even at a bulk concentration of 4.5 molal. We also observe that increasing the bulk concentration of formate/acetate leads to a shift of the vibrational bands to higher frequencies, and an increasing asymmetry of the band shape. This change of the spectral shape and position

is most clearly seen for the ν_{as} band and can be explained by the change of the refractive index which in turn affects the Fresnel factors. We modeled the VSFG response of the ν_s and ν_{as} vibrations using a three-layer model, combined with a Lorentz model to calculate the change of the refractive index of the interfacial layer with increasing carboxylate concentration.^{37,38} In Figure 4 we compare the experimental and calculated VSFG responses for an aqueous solution of sodium acetate at different concentrations. At high ion concentrations, the infrared refractive index and the Fresnel factor of the infrared light acquire a strong frequency dependence due to the vibrational resonances. This change of the Fresnel factor leads to an increase of the high-frequency wings of the responses of the ν_s vibrations and ν_{as} vibrations. As a result, the bands become asymmetric and the maxima shift to higher frequencies. It is also observed that the band of the ν_{as} vibration is more affected than the band of the ν_s vibration. This can be explained from the higher infrared cross-section of the ν_{as} vibration, which induces a stronger frequency dependence of the refractive index and the Fresnel factor at frequencies close to this vibration. We also modeled the VSFG response of aqueous sodium acetate solutions at different concentrations also with the two-layer model, and we find that this model clearly overestimates the Fresnel effects on the VSFG spectrum (see Figure 10 of Supporting Information). A detailed description of the two models and the determination of the Fresnel factors can be found elsewhere.³⁷⁻³⁹ We conclude that the three-layer model accounts very well for the experimentally observed changes in spectral shape and position. This means that these changes can be fully explained by Fresnel effects and are not caused by changes in the direct molecular environment of formate and acetate, e.g. changes in hydrogen-bond strength or configuration when increasing the carboxylate concentration.

Previous surface tension measurements by Minofar *et al.* show that for aqueous acetate solutions a clear decrease in surface tension is observed with increasing concentration, indicating that acetate is surface-active.^{25,26} These surface tension measurements are accompanied by MD simulations, yielding the density profile of the carboxylate ion near the surface. For acetate it is found that the density is enhanced compared to that of water at the surface, meaning that this ion has a clear surface propensity.^{25,26} In addition, the MD simulations show that the acetate ions are oriented with their carboxylate groups pointing toward the bulk. Our observation of a strong positive ν_s band in the HD-VSFG spectrum of aqueous acetate, agrees well with the results of these previous surface tension measurements and MD simulations.^{25,26} Interestingly, in the same study it is found that the addition of sodium formate does not lead to a significant change of the surface tension.²⁶ The accompanying MD simulations show that the density at the surface of formate is lower than that of water, and that the formate ions do not have a preferred orientation.²⁶ The latter result is not in agreement with our observations. The HD-VSFG spectrum of formate shown in Figure 2, in particular the positive ν_s vibrational band, show that formate has a net orientation of its carboxylate group toward the bulk, albeit that the SPS data show that the degree of orientation is not very strong and less than that of acetate. The fact that the addition of sodium formate does not significantly change the surface tension also indicates that formate is present at the surface, probably showing a very similar dependence of its density

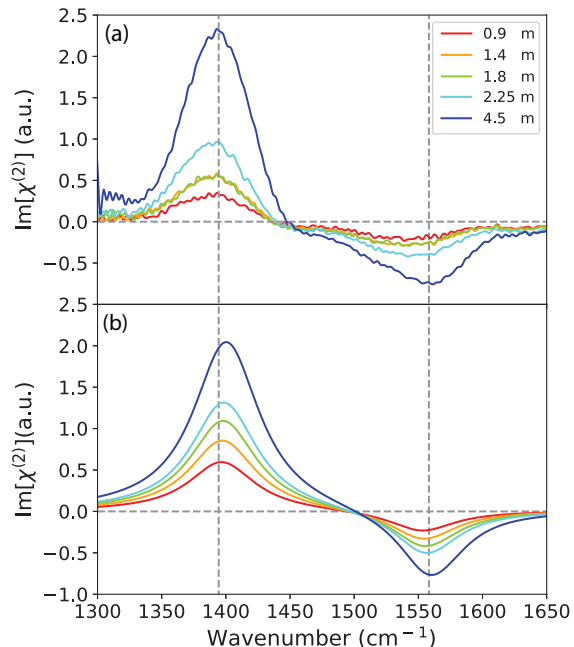


Figure 4. (a) Experimental and (b) calculated $\text{Im}[\chi^{(2)}]$ spectra of aqueous sodium acetate solutions for different concentrations in the concentration range of 0.9 - 4.5 m. The calculated $\text{Im}[\chi^{(2)}]$ spectra are obtained by accounting for the effect of acetate on the infrared Fresnel factors using the three-layer model, as described in the text and the Supplementary Information.

profile on the depth into the solution as water.

In conclusion, we performed Fourier Transform Infrared (FTIR) absorption and heterodyne-detected vibrational sum frequency generation (HD-VSFG) measurements of aqueous sodium formate and sodium acetate solutions. The HD-VSFG spectra contain responses of both the symmetric (ν_s) and the antisymmetric (ν_{as}) vibrations of the carboxylate group. The ν_s band has a positive sign which shows that formate and acetate both have a net orientation with their carboxylate group pointing toward the bulk. The observation of the ν_{as} band in the HD-VSFG spectrum of the formate and acetate solution and additional HD-VSFG measurements performed in SPS polarization configuration show that the c-axis of these ions is at a nonzero angle with respect to the surface normal. From the amplitudes of the ν_{as} bands and the SPS measurements it follows that this angle is smaller for acetate than for formate. We find that the amplitudes of both vibrational bands increase linearly with bulk concentration up to concentrations of 4.5 m. This finding implies that, even at these high bulk concentrations, the surface is not getting saturated with carboxylate ions, and that there is no significant change of the orientation angle of the formate and acetate ions. Finally, we found that at high carboxylate concentrations the ν_s and ν_{as} bands in the HD-VSFG spectrum become asymmetric and shift to higher frequencies, which can be quantitatively explained from the change of the Fresnel factor of the infrared beam.

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Supporting Information Available

FTIR spectra of sodium acetate and sodium formate solutions in D₂O ranging from 1.0 to 4.5 m in 1150-1700 cm⁻¹ frequency region; calculated complex refractive index and Fresnel factors in 1300-1650 cm⁻¹ frequency region; FTIR spectra of 4.5 m sodium acetate and 4.5 m sodium formate solutions in 2750 - 3100 cm⁻¹; Im[χ⁽²⁾] spectra of the neat water surface and aqueous formate/acetate solution with a concentration of 4.5 m in H₂O and D₂O.; Im[χ⁽²⁾] spectra of 2.5 m sodium acetate and 4.5 m sodium formate solutions in D₂O in SPS polarization combinations compared to SSP polarization combination and quantitative analysis of the orientation of carboxylate group at the water/air interface; model of the effect of the Fresnel-Factors on the ν_s and ν_{as} vibrations of the carboxylate group for increasing concentrations.

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