THE JOURNAL OF
PHYSICAL CHEMISTRY C

Subscriber access provided by FOM INSTITUUT VOOR ATOOM EN

Article

Strong Isotope Effect in the Vibrational Response of the Hydration Shells of Hydrophobic Ions

Liyuan Liu, Simona Strazdaite, and Huib J. Bakker

J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.5b06220 • Publication Date (Web): 15 Oct 2015

Downloaded from http://pubs.acs.org on November 23, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

The Journal of Physical Chemistry C is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Strong Isotope Effect in the Vibrational Response of the Hydration Shells of Hydrophobic Ions

Liyuan Liu,* Simona Strazdaite, and Huib J. Bakker

FOM Institute for Atomic and Molecular Physics, Science Park 104, 1098 XG Amsterdam, The Netherlands

E-mail: l.liu@amolf.nl

Abstract

We study the properties of water molecules at the surface of salt solutions containing hydrophobic anions like triflate ($CF_3SO_3^-$), ethanesulfonate ($C_2H_5SO_3^-$), and butanesulfonate ($C_4H_9SO_3^-$) using vibrational sum-frequency generation (VSFG) spectroscopy. The VSFG spectra reveal a surprisingly strong isotope effect in the intra- and intermolecular mixing of the water molecules contained in the hydration shells of the hydrophobic anions. The O–H stretch vibrations of H_2O molecules in the hydration shell are strongly mixed whereas the O–D stretch vibrations of hydrating D_2O molecules are decoupled. This isotope effect is not observed for other ions like perchlorate (ClO_4^-), and can be explained from the enhanced tetrahedral structure organization of the hydration shells of the hydrophobic ions.

Introduction

The addition of inorganic salts leads to an increase of the surface tension of water, which implies that the ions avoid the surface. However, this notion only concerns the average concentration of

---

*To whom correspondence should be addressed cations and anions, it does not imply that the concentrations of cations and anions would show a gradual decrease towards the interface. Molecular dynamics simulations showed that the concentrations of halogenic anions show large irregularities close to the interface.[1,2] According to these simulations, weakly hydrated anions like Br^- and I^- show an excess concentration at the water-air interface, whereas strongly interacting ions like F^- ion are excluded from this interface. These predictions were confirmed in several experiments, including studies using surface second harmonic generation (SHG), vibrational surface sum-frequency generation (VSFG) spectroscopy, soft X-ray photoelectron spectroscopy, and even atmospheric chemical reactions.[3–8]

The technique of VSFG has also been used to study the surface propensity of more complex inorganic ions like ammonium ($NH_4{}^+$), nitrate($NO_3{}^-$), sulfate ($SO_4{}^-$), thiocyanate (SCN^-) and perchlorate $ClO_4{}^-$.[9–11] In all these studies the surface propensity was found to depend strongly on the strength of the interaction between the ion and water. Ions that show a weak interaction with water like perchlorate have the highest surface propensity. The surface propensity of inorganic ions thus closely follows the Hofmeister series.

The surface propensity of ions can be strongly enhanced by introducing hydrophobic groups to the ions.[12] Ions containing large hydrophobic groups, like stearate and palmitate, have such a high surface propensity that they lower the surface tension of liquid water, meaning that these ions are surfactants. In this work, we study the vibrational response of the water molecules contained in the hydration shells of the hydrophobic anions triflate ($CF_3SO_3{}^-$), ethanesulfonate ($C_2H_5SO_3{}^-$) and butanesulfonate ($C_4H_9SO_3{}^-$) using conventional vibrational sum frequency generation (VSFG) spectroscopy and phase sensitive vibrational sum frequency generation (PS-VSFG) spectroscopy. The measurements reveal a surprisingly strong isotope effect in the intra- and intermolecular interaction of the hydroxyl stretch vibrations of the water molecules in the hydrations shells of these ions.

Experiment

In vibrational sum-frequency generation (VSFG) spectroscopy a visible and a broadband infrared pulse are combined at the surface to generate light at the sum-frequency. The sum-frequency generation process will be enhanced in case the infrared light is resonant with a molecular vibration. VSFG spectroscopy is highly surface specific thanks to the fact that the technique is symmetry forbidden in media that show inversion symmetry (within the dipole approximation). The intensity of the VSFG signal is proportional to:

$$I_{\mathrm{SFG}}(\omega_3) \propto |\chi^{(2)}(\omega_3 = \omega_2 + \omega_1)|^2 I_{\mathrm{vis}}(\omega_2) I_{\mathrm{IR}}(\omega_1), \tag{1}$$

with ω_3 the frequency of the sum-frequency light, ω_2 the frequency of the visible light, ω_1 the frequency of the infrared light, and $\chi^{(2)}(\omega_3 = \omega_2 + \omega_1)$ the resonantly enhanced second-order susceptibility. We generate infrared and visible pulses with a regenerative Ti:Sapphire amplifier system (see supporting information). The generated narrow-band 800 nm and broad-band infrared pulses are sent onto the sample surface in temporal and spatial overlap, and produce light at the sum frequency. We used infrared and visible pulse energies of 10 and 15 μJ, respectively. The generated sum-frequency light is sent into a monochromator and detected with an Electron-Multiplied Charge Coupled Device (EMCCD, Andor Technologies). All spectra are recorded with s-polarised SFG, s-polarised 800 nm, and p-polarised infrared light (with respect to the plane of incidence).[13] The SFG spectra of the solutions in H_2O are obtained by integrating the signal for 10 minutes, and the SFG spectra of the solutions in D_2O are obtained by integrating the signal for 4 minutes.

In conventional VSFG spectroscopy the intensity of the sum-frequency light is plotted as a function of the infrared frequency ω_1. This intensity is proportional to the squared amplitude of the complex second-order nonlinear susceptibility $\chi^{(2)}(\omega_3 = \omega_2 + \omega_1)$. Information on the phase and sign of $\chi^{(2)}$ can be obtained by interfering the sum-frequency light coming from the sample with sum-frequency light coming from a local oscillator. We perform such a phase-sensitive VSFG (PS-VSFG) experiment by sending the infrared and 800 nm beams first on a gold mirror to generate broadband light at the sum frequency (local oscillator). Subsequently, the three beams (infrared, 800 nm and sum-frequency light) are sent together onto the salt solution to generate the sample sum-frequency light. The sum-frequency light beam that is generated at the gold mirror is delayed by a time $\Delta\tau$ by sending this beam through a tilted fused silica plate. The sum-frequency light generated at the gold mirror and the sum-frequency light generated at the sample co-propagate to the spectrograph and are detected by the CCD camera. The detected intensity is given by:

$$\begin{aligned} I_{\mathrm{PS-VSFG}}(\omega_3) \propto & \|E_{sample}(\omega_3)\|^2 + \|E_{LO}(\omega_3)\|^2 \\ & + E^*_{sample}(\omega_3)E_{LO}(\omega_3)e^{i\omega_3\Delta\tau} + E_{sample}(\omega_3)E^*_{LO}(\omega_3)e^{-i\omega_3\Delta\tau} \end{aligned} \qquad (2)$$

The cross-term $E_{sample}E^*_{LO}e^{-i\omega_3\Delta\tau}$ contains the electric field of the sum-frequency light originating from the sample and is directly proportional to the complex $\chi^{(2)}$.

The studied salts sodium triflate, sodium ethanesulfonate, sodium butanesulfonate and sodium perchlorate are all purchased from Sigma-Aldrich and are used without further purification. The purity of all chemicals is $\geq$ 98%. The salts are dissolved in H_2O (>99.9%) and D_2O (>99.9%) in a series of concentrations that are indicated with molar fractions x =[salt]/([salt]+[water]). To avoid H/D exchange between the salt solutions in D_2O and water vapor, we flushed the infrared generation and the VSFG signal generation and detection part of the setup with nitrogen gas. We measured IR spectra of the solutions using a commercial Fourier Transform Infrared (FTIR) spectrometer (FTS175 Biorad). In these measurements the samples are contained between two CaF_2 windows (2 mm thick) that are separated by a 3 μm Teflon spacer.

Results and discussion

Figure 1 shows VSFG spectra of sodium triflate solutions at different molar fractions. The spectrum of pure H_2O shows a broad double band structure with maxima at 3200 and 3400 cm^{-1}, and an additional peak at ~3700 cm^{-1}. The double band has been assigned to O–H stretch vibrations forming hydrogen bonds to other water molecules. The structure of this band has been explained

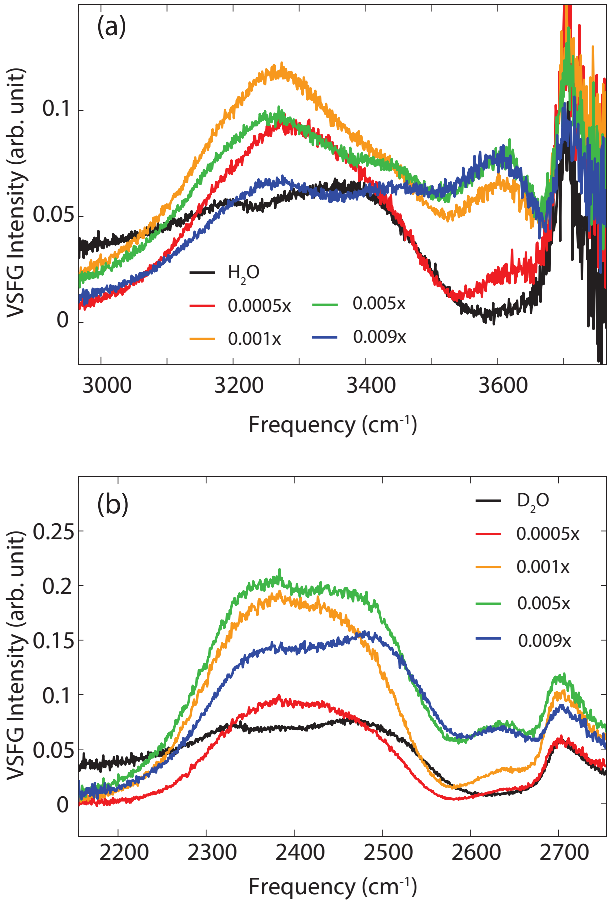

Figure 1: Vibrational sum frequency generation (VSFG) spectra of solutions of sodium triflate ($NaCF_3SO_3$) at different molar fractions x. (a) in H_2O and (b) in D_2O

from the near-resonant intra- and intermolecular coupling of the O–H stretch vibrations, and the coupling of the O–H stretch vibrations with the overtone of the bending mode.[14] The band at $\sim$3700 cm^{-1} has been assigned to the stretch vibrations of non-hydrogen-bonded O–H groups that are sticking out of the surface. The VSFG spectrum of pure D_2O has a very similar shape. The hydrogen-bonded O–D stretch vibrations give rise to a broad-band feature with maxima at 2360 and 2500 cm^{-1} and the dangling O–D groups give rise to the narrow band at $\sim$2700 cm^{-1}.

The addition of sodium triflate leads to an additional band in the VSFG spectrum at $\sim$3600/2640 cm^{-1} for solutions in H_2O/D_2O. The amplitude of this band increases with increasing mole fraction of sodium triflate. We assign this band to a hydroxyl group forming a hydrogen bond to the sulfonate group of the $CF_3SO_3{}^-$ anion. This hydrogen bond is weak, which explains the relatively high frequency of the hydroxyl stretch vibration. The additional band at $\sim$3600/2640 cm^{-1} is already observed at mole fractions of 0.0002, corresponding to a bulk concentration of 10 mM, which implies that the triflate anion shows a high surface propensity, which is a direct consequence of its hydrophobic nature. The addition of sodium triflate also changes the shape and amplitude of the double band structure associated with the O–H/O–D groups forming hydrogen bonds to H_2O/D_2O molecules. Interestingly, these changes depend on whether the salt is dissolved in H_2O or D_2O. In the case of H_2O the addition of sodium triflate leads to a blue shift of the double band and an increase in amplitude, whereas for D_2O the addition of sodium triflate leads to a minor change of the frequency position of the double band and an even stronger increase in amplitude.

In Figure 2 we present VSFG spectra of solutions of sodium butanesulfonate ($NaC_4H_9SO_3$) in H_2O and D_2O. The butanesulfonate anion has the same sulfonate anionic group as triflate and only differs from the triflate anion in the character of the hydrophobic group. The addition of sodium butanesulfonate leads to very similar changes of the VSFG spectrum as the addition of sodium triflate (Figure 1). As in the case of sodium triflate, these changes occur already at low molar fractions of sodium butylsulfonate, which shows that butanesulfonate anions have a high surface propensity. The high surface propensity of butanesulfonate anions is also demonstrated by the clear observation of CH_2 and CH_s stretch vibrational bands in the VSFG spectrum at low bulk

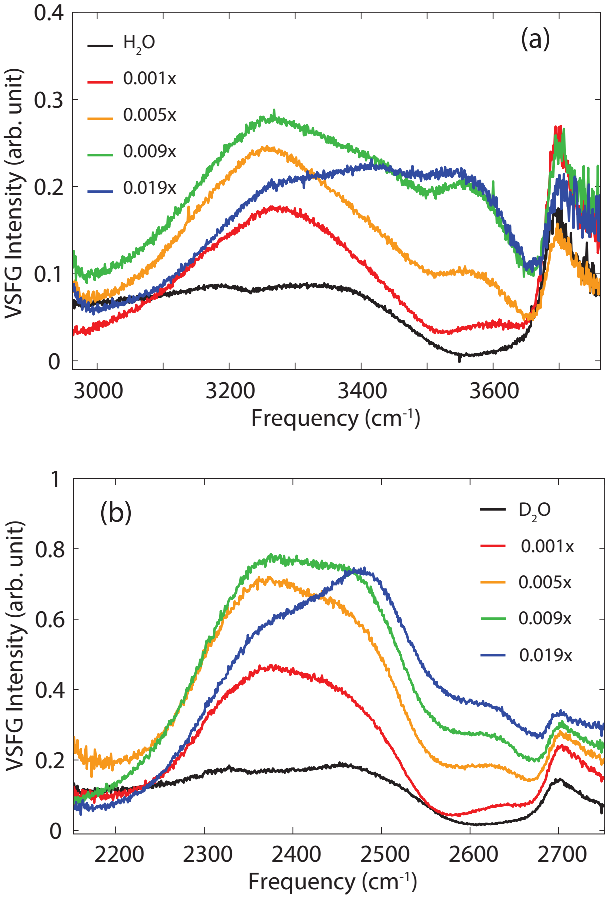

Figure 2: Vibrational sum frequency generation (VSFG) spectra of solutions of sodium butanesulfonate ($NaC_4H_9SO_3$) at different molar fractions x. (a) for solutions in H_2O and (b) in D_2O

concentrations (see supporting information). The spectral changes in the frequency region of the O–H/O–D groups forming hydrogen bonds to H_2O/D_2O show again a strong isotope effect. Similar effects are observed for solutions of sodium ethanesulfonate ($NaC_2H_5SO_3$) (see Supplementary Information).

We performed PS-VSFG experiments to study the effect of hydrophobic anions on the O–H and O–D stretch vibrations in more detail. In Figure 3 we present the measured Im($\chi^{(2)}$) as a function of frequency for sodium triflate solutions of different concentration in H_2O and D_2O. For comparison we also present Im($\chi^{(2)}$) of the water-air interfaces of pure H_2O and D_2O. The sign of the imaginary part of the second-order susceptibility Im($\chi^{(2)}$) directly reflects the orientation of the transition dipole moments of the interfacial O–D/O–H vibrations.[15–18] A positive imaginary $\chi^{(2)}$ corresponds to O–H/O–D groups pointing towards air. For pure H_2O/D_2O Im($\chi^{(2)}$) has a small positive value at hydroxyl stretch vibrational frequencies $<$3100/2300 cm^{-1}. These hydroxyl stretch vibrations correspond to strongly hydrogen-bonded O–H/O–D groups. The main part of Im($\chi^{(2)}$) between 3100 and 3600 cm^{-1} for H_2O and between 2300 and 2600 cm^{-1} for D_2O, has a negative sign, indicative of a net orientation towards the water phase. Finally, Im($\chi^{(2)}$) of the dangling O–H/O–D groups is positive, in line with the fact that these groups are sticking out of the H_2O/D_2O surface.

The addition of sodium triflate leads to a large change in the amplitude and sign of Im($\chi^{(2)}$). The dominant negative part of pure H_2O/D_2O completely disappears and gives way to a strong positive Im($\chi^{(2)}$). This change in sign of Im($\chi^{(2)}$) reflects a change in the net orientation of the hydroxyl groups. This change in net orientation can be explained from the difference in surface propensity between the negative triflate anions and the positive sodium cations. The hydrophobic triflate anions have a strong tendency to accumulate at the water-air interface, whereas the sodium cations remain further away from this interface. This separation of positive and negative charge near the water-air interface yields a strong local electric field that orients the O–H/O–D groups towards the interface, thus resulting in a positive Im($\chi^{(2)}$). The mole fraction of sodium triflate at which Im($\chi^{(2)}$) becomes positive at all frequencies is approximately x=0.0005 ($\approx$25 mM), both

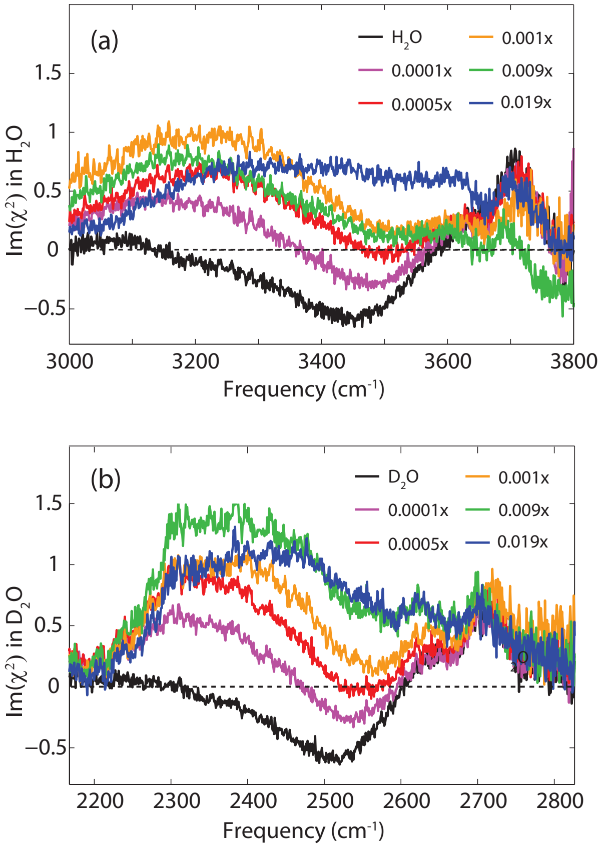

Figure 3: Imaginary part of the second-order susceptibility $\chi^{(2)}$ of sodium triflate ($NaCF_3SO_3$) solutions at different molar fractions x. (a) in H_2O and (b) in D_2O. The imaginary $\chi^{(2)}$ is determined with PS-VSFG spectroscopy.

for H_2O and for D_2O. This similarity in concentration indicates that the triflate anions show a similar surface propensity in H_2O and D_2O. Hence, there appears to be no isotope effect in the surface propensity of triflate. Nevertheless, at higher triflate concentrations the frequency position and amplitude of Im($\chi^{(2)}$) strongly differs for H_2O and D_2O. For H_2O Im($\chi^{(2)}$) is much more strongly blue shifted than for D_2O, whereas for D_2O the amplitude of the positive Im($\chi^{(2)}$) is more enhanced than for H_2O. These observations agree with the results of the intensity VSFG spectra of Figure 1.

Figure 1, Figure 2 and Figure 3 clearly show that the addition of triflate and butanesulfonate has a quite different effect on the VSFG spectrum for solutions in H_2O than for solutions in D_2O. This strong isotope effect can be explained from the difference in strength of the intramolecular and intermolecular (Förster) dipole-dipole interactions of the hydroxyl vibrations of H_2O and D_2O. For pure H_2O and pure D_2O the near-resonant intramolecular and intermolecular interactions lead to a strong mixing of the local hydroxyl vibrations and a delocalization of the hydroxyl stretch vibrations. As a result, the first excited state of the O–H/O–D vibration is a delocalized exciton state that comprises several local O–H/O–D excitations.[19–21]

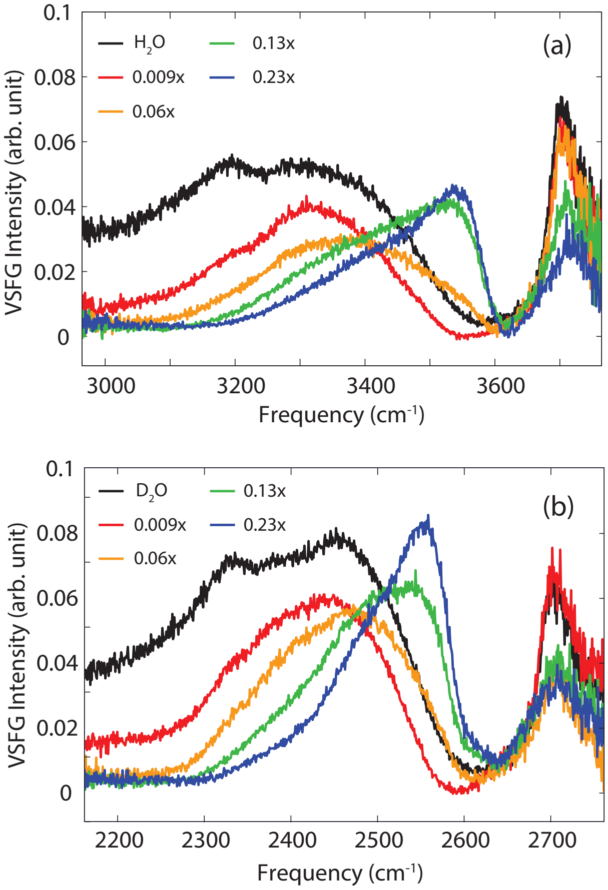

Figure 4: Vibrational sum frequency generation (VSFG) spectra of solutions of sodium perchlorate ($NaClO_4$) at different molar fractions x.(a) in H_2O and (b) in D_2O.

For solutions of triflate, ethanesulfonate and butanesulfonate in H_2O, the intra- and intermolecular couplings lead to the formation of delocalized vibratonial exciton states that include both O–H groups forming hydrogen bonds to H_2O molecules and O–H groups that form weak hydrogen bonds to the sulfonate group. These exciton states will be blue shifted in comparison to the exciton states of pure H_2O. The absence of such a blue shift for solutions of these hydrophobic anions in D_2O indicates that the O–D stretch vibrations are far less mixed than the O–H stretch vibrations.

The amount of mixing of O–H/O–D vibrations depends both on the interaction energy and the difference in site energy. Substantial mixing occurs when the interaction energy exceeds the differences in site energies. Going from H_2O to D_2O the intra- and intermolecular interaction energies and the differences in site energies will decrease. The intramolecular and intermolecular interaction energies are both proportional to the product of the transition dipole moments of the coupled hydroxyl stretch vibrations. The transition dipole moment of the O–H stretch vibration is $\sim\sqrt{2}$ larger than that of the O–D stretch vibration, and thus the interaction energy will be ~ 2 times larger for H_2O than for D_2O. The smaller interaction energy of D_2O corresponds to a lower rate of near-resonant energy transfer between local O–D stretch vibrations. Indeed this rate was measured to be >2 times smaller for D_2O than for H_2O.[19–21] Going from H_2O to D_2O the differences in site energies, i.e. the differences in local hydroxyl vibrational frequencies, are expected to decrease by a factor $\sim\sqrt{2}$. The isotope effect of the site energy differences is thus smaller than the isotope effect of the intra- and intermolecular interactions. This difference in isotope effect explains why the water-bound and anion-bound hydroxyl vibrations are well mixed in solutions of triflate, ethanesulfonate and butanesulfonate in H_2O and poorly mixed in solutions of these anions in D_2O.

From the above it is clear that the amount of mixing of water-bound and anion-bound hydroxyl vibrations is a subtle effect that depends on the distribution of the local site energies of the hydroxyl vibrations. To study this effect in more detail we measured VSFG spectra of solutions of other salts in H_2O and D_2O. In Figure 4 we show VSFG spectra of solutions of sodium perchlorate in H_2O and D_2O. The addition of sodium perchlorate is also seen to lead to an additional band in the spectrum at a relatively high frequency, as was the case for the triflate, ethanesulfonate and butanesulfonate solutions (Figure 1 and Figure 2). Following the work of the group of Allen we assign this band at 3560 cm^{-1}/2570 cm^{-1} to O–H/O–D groups forming hydrogen bonds to the perchlorate (ClO_4^-) anions.[9] These hydrogen bonds are weak and probably directed towards the

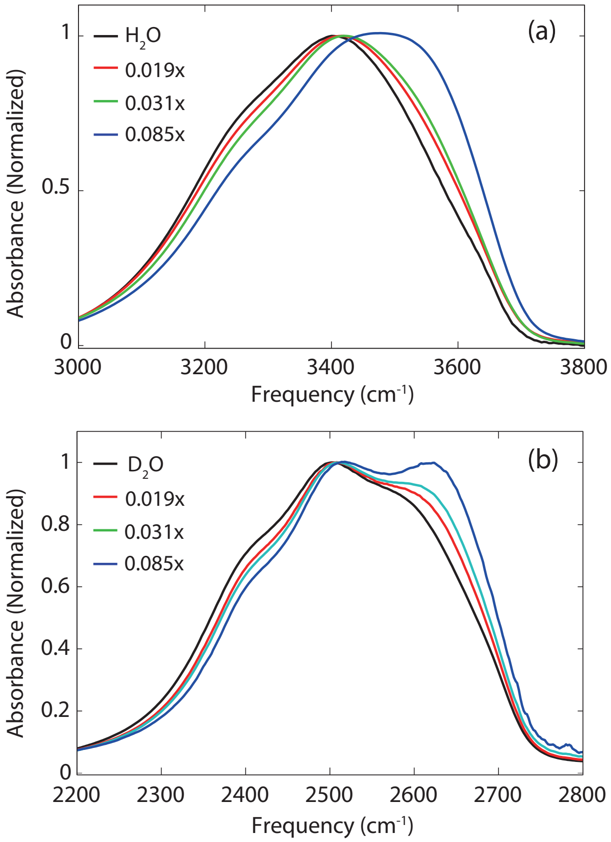

Figure 5: Infrared absorption spectra of solutions of sodium triflate ($NaCF_3SO_3$) in H_2O (a), in D_2O (b).

middle of the O-O ridges of the tetrahedral perchlorate anion.[22] The changes of the VSFG spectrum induced by perchlorate are quite similar for H_2O and D_2O. For both solvents the VSFG spectrum of the broad double band shows a blue shift and a decrease in amplitude. Hence, the isotope effect on the shape of the VSFG spectrum of perchlorate solutions is small, in strong contrast to the VSFG spectra of solutions of triflate (Figure 1), ethanesulfonate (supporting information), and butanesulfonate (Figure 2).

The results of Figure 4b show that for solutions of sodium perchlorate in D_2O the stretch vibrations of O–D groups donating hydrogen bond to D_2O are quite well mixed with the stretch vibrations of O–D groups donating hydrogen to ClO_4^-. This finding implies that for ClO_4^- the intra- and intermolecular interaction energy is sufficiently large to overcome the differences in local frequencies of the O–D stretch vibrations. As the transition dipole moments are not very different, it thus appears that for ClO_4^- the stretch vibration of the O–D group donating a hydrogen bond to the anion is closer in frequency to the stretch vibrations of other nearby O–D groups than for triflate, ethanesulfonate and butanesulfonate. This can be due to two effects. The first effect is that the frequency of O–D group donating a hydrogen bond to the anion is somewhat less blue shifted for perchlorate than for the studied hydrophobic anions. A second effect is that the stretch frequencies of other nearby O–D groups that form hydrogen bonds to D_2O would be lower in the case of the studied hydrophobic anions than in the case of perchlorate. It has been found that water molecules hydrating hydrophobic groups have an enhanced tetrahedral hydrogen-bonded structure which implies that their vibrational spectrum will be redshifted and narrower compared to that of water molecules in bulk liquid water.[23] Hence the O–H/O–D groups that donate a hydrogen bond to an H_2O/D_2O molecule in the hydrophobic hydration shell of triflate, ethanesulfonate and butanesulfonate can have frequencies that are quite strongly redshifted with respect to the O–H/O–D groups that donate a hydrogen bond to the sulfonate group of these hydrophobic anions. In the case of D_2O, this large frequency difference in combination with the weaker interaction energy, precludes the mixing of the O–D stretch vibrations in the hydration shell of the hydrophobic anion. For H_2O, the interaction energy still suffices to mix the O–H stretch vibrations of the H_2O molecules hydrating the hydrophobic part with the O–H stretch vibrations of the hydroxyl groups donating a weak hydrogen bond to the sulfonate group.

We also measured bulk IR absorption spectra of solutions of sodium triflate and sodium perchlorate in H_2O and D_2O to investigate whether the differences in vibrational response are specific for the water surface. The results are shown in Figure 5. It is seen that the IR spectra show very similar trends as the VSFG spectra. The addition of sodium triflate leads to a stronger blue shift of the band at 3400/2500 cm^{-1} for solutions in H_2O than for solutions in D_2O. This shows again that the stretch vibrations of the anion-bound and water-bound hydroxyl groups are more strongly mixed for solutions in H_2O than for solutions in D_2O. The poor mixing of anion-bound and D_2O-bound O–D vibration in the hydration shells of triflate thus persists in the bulk.

Solutions of triflate, ethanesulfonate and butanesulfonate do not only show a strong isotope effect in the frequency position of the bands but also in the amplitude. The addition of these anions to D_2O leads to a rather strong increase in amplitude of the main band of the VSFG spectrum, whereas for H_2O the amplitude of this band hardly changes. This isotope effect can also be explained from the difference in mixing of the anion- and water-bound hydroxyl vibrations for H_2O and D_2O. The addition of triflate, ethanesulfonate and butanesulfonate or butanesulfonate to H_2O and D_2O affects the amplitude in different ways. In the first place, the static electric field E_{st} resulting from the accumulation of anions at the surface increases the orientation of O–H/O–D groups towards the interface, thus enhancing the VSFG signal. This orientation effect is clearly seen in the increase of Im($\chi^{(2)}$) shown in Figure 3. The static electric field E_{st} can further change Im($\chi^{(2)}$) through a field-induced $\chi^{(2)}$ (=$E_{st}\chi^{(3)}$ contribution.[24,25] This effect involves the polarization of the electron cloud and is expected to be small compared to the change in amplitude and sign of Im($\chi^{(2)}$) associated with the change in net orientation of the water molecules induced by E_{st}. Second, the accumulation of hydrophobic anions ions at the interface will lead to a decrease of the density of H_2O/D_2O molecules which decreases the VSFG signal. These two effects will be similar for H_2O and D_2O. For H_2O a third effect is formed by the mixing of the O–H groups forming hydrogen bonds to H_2O with O–H groups bonded to the anion. This mixing leads to the formation of new delocalized states with a large frequency spread and a weaker average hydrogen-bond strength which decreases the associated VSFG signal. This latter effect will be small for D_2O as the O–D groups forming hydrogen bonds to D_2O poorly mix with O–D groups forming hydrogen bonds to the anion. As a result, the average hydrogen bond strength and thus the cross-section of the O–D vibrations in the main VSFG band remains large. Hence, for D_2O the main band of the VSFG spectrum increases in amplitude because of the orienting electric field created by the anions at the interface, whereas for H_2O the main band hardly changes in amplitude because the orientation effect is counteracted by the deteriorating effects of mixing on the cross-section.

Conclusions

We studied the vibrational response of water molecules at the surface of solutions containing hydrophobic anions using vibrational surface sum-frequency generation (VSFG) spectroscopy. The addition of ions like triflate ($CF_3SO_3{}^-$), ethanesulfonate ($C_2H_5SO_3{}^-$), butanesulfonate ($C_4H_9SO_3{}^-$) is observed to lead to the rise of a high-frequency resonance at $\sim$3600/2640 cm^{-1} that is assigned to the stretch vibration of an O–H/O–D group forming a weak hydrogen bond to the anion. This additional band is already observed at a low mole fraction of x=0.0002 (corresponding to a concentration of 10 mM), which shows that these ions have a very high surface propensity.

The addition of triflate, ethanesulfonate, and butanesulfonate strongly affects the frequency position and amplitude of the main band of the VSFG spectrum of H_2O/D_2O. For solutions in H_2O, the addition of these hydrophobic anions is observed to lead to a strong blueshift of the main band of the VSFG spectrum and little change in amplitude, whereas for solutions in D_2O the addition of these anions hardly changes the frequency position of the main band but leads to a strong increase in amplitude.

This strong isotope effect can be explained from the difference in intra- and intermolecular coupling of O–H and O–D vibrations in the hydration shells of the hydrophobic anions. The intra- and intermolecular coupling of water hydroxyl vibrations scales with the product of the transition dipole moments of the coupled stretch vibrations, which means that this interaction is $\sim$2 times larger in H_2O than in D_2O. As a result, O–H groups forming hydrogen bonds to H_2O show significant mixing with O–H groups forming weak hydrogen bonds to the sulfonate group of triflate, ethanesulfonate or butanesulfonate, whereas for the O–D groups in D_2O this mixing is poor. This isotope effect is not observed for other ions like perchlorate, which can be explained from the enhanced tetrahedral structure of water hydrating hydrophobic groups. As a result of the enhanced structure, the stretch vibrations of the hydroxyl groups hydrating the hydrophobic part of the ion have low and well-defined vibrational frequencies, which in the case of D_2O precludes their mixing with the high-frequency stretch vibrations of the hydroxyl group hydrating the sulfonate group of the ion. For H_2O, the interaction energy still suffices to mix the O–H stretch vibrations of the H_2O molecules hydrating the hydrophobic part with the O–H stretch vibrations of the hydroxyl groups donating a weak hydrogen bond to the sulfonate group.

Acknowledgment

This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the “Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO)". The authors thank Sander Woutersen for useful discussions and Hinco Schoenmaker for technical support.

Supporting Information Available

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Additional informations on vibrational sum-frequency generation (VSFG) spectroscopy setup. VSFG Spectrum of Sodium Butanesulfonate Solutions in C–H region.

References

[1] Jungwirth, P.; Tobias, D. J. Molecular Structure of Salt Solutions: A New View of the Interface with Implications for Heterogeneous Atmospheric Chemistry. *J. Phys. Chem. B* **2001**, *105*, 10468–10472.

[2] Mucha, M.; Frigato, T.; Levering, L. M.; Allen, H. C.; Tobias, D. J.; Dang, L. X.; Jungwirth, P. Unified Molecular Picture of the Surfaces of Aqueous Acid, Base, and Salt Solutions. *J. Phys. Chem. B* **2005**, *109*, 7617–7623.

[3] Liu, D.; Ma, G.; Levering, L. M.; Allen, H. C. Vibrational Spectroscopy of Aqueous Sodium Halide Solutions and Air–Liquid Interfaces: Observation of Increased Interfacial Depth. *J. Phys. Chem. B* **2004**, *108*, 2252–2260.

[4] Petersen, P. B.; Saykally, R. J.; Mucha, M.; Jungwirth, P. Enhanced Concentration of Polarizable Anions at the Liquid Water Surface: SHG Spectroscopy and MD Simulations of Sodium Thiocyanide. *J. Phys. Chem. B* **2005**, *109*, 10915–10921.

[5] Raymond, E. A.; Richmond, G. L. Probing the Molecular Structure and Bonding of the Surface of Aqueous Salt Solutions. *J. Phys. Chem. B* **2004**, *108*, 5051–5059.

[6] Ottosson, N.; Cwiklik, L.; Söderström, J.; Björneholm, O.; Öhrwall, G.; Jungwirth, P. Increased Propensity of I^-_{aq} for the Water Surface in Non-neutral Solutions: Implications for the Interfacial Behavior of $H_3O^+_{aq}$ and OH^-_{aq}. *J. Phys. Chem. Lett.* **2011**, *2*, 972–976.

[7] Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. Reactive Uptake of Cl_2(g) and Br_2(g) by Aqueous Surfaces as a Function of Br^- and I^- Ion Concentration: The Effect of Chemical Reaction at the Interface. *J. Phys. Chem.* **1995**, *99*, 8768–8776.

[8] Laskin, A.; Gaspar, D. J.; Wang, W.; Hunt, S. W.; Cowin, J. P.; Colson, S. D.; Finlayson-Pitts, B. J. Reactions at Interfaces As a Source of Sulfate Formation in Sea-Salt Particles. *Science* **2003**, *301*, 340–344.

[9] Hua, W.; Verreault, D.; Allen, H. C. Surface Prevalence of Perchlorate Anions at the Air/Aqueous Interface. *J. Phys. Chem. Lett.* **2013**, *4*, 4231–4236.

[10] Tian, C.; Byrnes, S. J.; Han, H.-L.; Shen, Y. R. Surface Propensities of Atmospherically Relevant Ions in Salt Solutions Revealed by Phase-Sensitive Sum Frequency Vibrational Spectroscopy. *J. Phys. Chem. Lett.* **2011**, *2*, 1946–1949.

[11] Onorato, R. M.; Otten, D. E.; Saykally, R. J. Adsorption of Thiocyanate Ions to the Dodecanol/Water Interface Characterized by UV Second Harmonic Generation. *Proc. Natl. Acad. Sci.* **2009**, *106*, 15176–15180.

[12] Rao, Y.; Subir, M.; McArthur, E. A.; Turro, N. J.; Eisenthal, K. B. Organic Ions at the Air/Water Interface. *Chem. Phys. Lett.* **2009**, *477*, 241–244.

[13] Strazdaite, S.; Versluis, J.; Backus, E. H. G.; Bakker, H. J. Enhanced Ordering of Water at Hydrophobic Surfaces. *J. Chem. Phys.* **2014**, *140*, 054711.

[14] Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; MÃijller, M.; Bakker, H. J.; Bonn, M. Vibrational Response of Hydrogen-Bonded Interfacial Water is Dominated by Intramolecular Coupling. *Phys. Rev. Lett.* **2008**, *100*, 173901.

[15] Ji, N.; Ostroverkhov, V.; Chen, C.-Y.; Shen, Y.-R. Phase-Sensitive Sum-Frequency Vibrational Spectroscopy and Its Application to Studies of Interfacial Alkyl Chains. *J. Am. Chem. Soc.* **2007**, *129*, 10056–10057.

[16] Pool, R. E.; Versluis, J.; Backus, E. H. G.; Bonn, M. Comparative Study of Direct and Phase-Specific Vibrational Sum-Frequency Generation Spectroscopy: Advantages and Limitations. *J. Phys. Chem. B* **2011**, *115*, 15362–15369.

[17] Feng, R.-r.; Guo, Y.; Lü, R.; Velarde, L.; Wang, H.-f. Consistency in the Sum Frequency Generation Intensity and Phase Vibrational Spectra of the Air/Neat Water Interface. *J. Phys. Chem. A* **2011**, *115*, 6015–6027.

[18] Stiopkin, I. V.; Weeraman, C.; Pieniazek, P. A.; Shalhout, F. Y.; Skinner, J. L.; Benderskii, A. V. Hydrogen Bonding at the Water Surface Revealed by Isotopic Dilution Spectroscopy. *Nature* **2011**, *474*, 192–195.

[19] Woutersen, S.; Bakker, H. J. Resonant Intermolecular Transfer of Vibrational Energy in Liquid Water. *Nature* **1999**, *402*, 507–509.

[20] Cowan, M. L.; Bruner, B. D.; Huse, N.; Dwyer, J. R.; Chugh, B.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. Ultrafast Memory Loss and Energy Redistribution in the Hydrogen Bond Network of Liquid H_2O. *Nature* **2005**, *434*, 199–202.

[21] Piatkowski, L.; Bakker, H. J. Vibrational Relaxation Pathways of AI and AII Modes in N-Methylacetamide Clusters. *J. Phys. Chem. A 114*, 11462–11470.

[22] Walrafen, G. E. Raman Spectral Studies of the Effects of Perchlorate Ion on Water Structure. *J. Chem. Phys.* **1970**, *52*, 4176–4198.

[23] Davis, J. G.; Gierszal, K. P.; Wang, P.; Ben-Amotz, D. Water Structural Transformation at Molecular Hydrophobic Interfaces. *Nature* **2012**, *491*, 582–585.

[24] Jena, P. A. H. D. K., K. C.; Covert The Effect of Salt on the Water Structure at a Charged Solid Surface: Differentiating Second- and Third-order Nonlinear Contributions. *J. Phys. Chem. Lett.* **2011**, *2*, 1056–1061.

[25] Aktsipetrov, A. A. D. J. I. D. M. C., O. A.; Fedyanin DC-Electric-Field-Induced Second Harmonic Generation Studies of Surfaces and Buried Interface of Column IV Semiconductors. *Laser Phys.* **1996**, *6*, 1142–1151.

Graphical TOC