VIBRATIONAL SUM FREQUENCY SPECTROSCOPY STUDIES AT THE
AIR-LIQUID INTERFACE.

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“entre ordre et désordre...”
Abstract

ABSTRACT

In this thesis the structure and hydration of small organic and amphipilic compounds adsorbed at the air-liquid interface, have been studied using the nonlinear optical technique Vibrational Sum Frequency Spectroscopy (VSFS). The second order nature of the sum frequency process makes this technique particularly surface sensitive and very suitable for interfacial studies, as molecules at the surface can be distinguished even in the presence of a vast excess of the same molecules in the bulk. Particular emphasis was given to the surface water structure and how it is affected by the presence of small model compounds such as acetic acid and formic acid, and also non-ionic surfactants with sugar based and ethylene oxide based polar headgroups. Understanding the structure of water at these interfaces is of considerable fundamental importance, and here VSFS provided unique information. Upon addition of tiny amounts of these surface active compounds, the ordered surface structure of water was found to be significantly perturbed, as revealed by the changes observed in the characteristic spectroscopic signature of the dangling OH bond of water molecules, which vibrate free in air and are present in the top monolayer. Dramatic differences between the different compounds were also observed in the bonded OH region, providing a valuable insight into the hydration of polar groups at interfaces. Additionally, by employing different polarization combinations of the laser beams involved in the sum frequency process, information about the different water species present at the surface and their average orientation were extracted. In particular an unusual state of water was found with a preferred orientation in a non-donor configuration in close proximity to the hydrophobic region formed by the hydrocarbon tails of the surfactant molecules.

The conformation and orientation of the different adsorbates were also characterized, targeting their specific vibrational frequencies. Noteworthy is the orientation of the fluorocarbon chain of ammonium perfluorononanoate (APFN), which in contrast to the hydrocarbon chains of the other surfactant molecules studied, remained constant over a wide range of surface densities. This behaviour was also observed for the anionic headgroup of sodium dodecyl sulphate (SDS). Other interesting findings were the formation of a cyclic dimer bilayer at the surface of concentrated aqueous solutions of acetic acid and the water structuring effect induced by poly(ethylene-oxide) headgroups, in spite of being themselves disordered at the air-liquid interface.
SAMMANFATTNING

I den här avhandlingen har struktur och hydratisering av små organiska och amfifila ämnen adsorberade på luft/vätske-gränsytan studerats med hjälp av den ickelinjära, optiska tekniken "Vibrational Sum Frequency Spectroscopy" (VSFS). Denna teknik är särskilt ytkänslig och lämpad för studier av gränsytor p.g.a. den andra ordningens process som utgör grunden för tekniken. Molekyler vid en yta kan särskiljas även vid förekomsten av ett stort överskott av samma molekyler i bulklösningen eftersom ytmolekylerna har en nettoorientering (relativt ytnormalen). Särskild betoning har lagts vid ytstrukturen av vatten och på vilket sätt den påverkas av närvaron av små molekyler såsom ättiksyra och myrskyra, men även icke-joniska tensider med socker-, och etylenoxid-baserade polära huvudgrupper. Den grundläggande förståelsen av vattenstrukturerna vid dessa gränsytor är av stor betydelse, och inom detta område kan VSFS bidra med unik information. Även vid tillsats av minimala mängder ytaktiva ämnen påverkades den ordnade vattenstrukturen på ett anmärkningsvärt sätt, vilket påvisades genom spektroskopiska ändringar observerade för den fria OH-gruppen i vattenmolekyler i det översta monolagret. Påtagliga skillnader mellan olika ämnen observerades också i den spektrala regionen för vätebundna vattenmolekyler, vilket bidrar med värdefull insikt om hydratiseringen kring polära grupper vid fasgränsytor. Dessutom har information om vatten i olika typer av vätebindningsmiljöer och deras orientering kunnat bestämmas, genom att utföra experiment med olika polarisationer av laserstrålarna i summafrekvens-processen. Särskilt anmärkningsvärda är observationer av en speciell typ av vattenmolekyler som enbart ingår i vätebinding genom syreatomen, och befinner sig i närheten av den hydrofoba regionen i icke-joniska tensidskikt.

Konformationen och orienteringen av dessa olika ämnen har även undersökts genom mätningar kring deras egen-vibrationsfrekvenser. Nämnvärt är att orienteringen av den fluorinerade kolkedjan för ammoniumperfluorononatan (APFN) i kontrast till kolvätekedjorna för de andra tensiderna som studerats var konstant inom ett brett område av ytdensiteter. Detta beteende observerades också för den anjoniska huvudgruppen för natriumdodecylsulfat (SDS). Yttermära uptäcktes bildningen av biskikt bestående av cykliska dimerer i ytan vid höga koncentrationer av ättiksyra i vattenlösning. Slutligen undersöktes i detalj även den ordnade strukturen av vattenmolekyler som kringgärdar tensidhuvudgrupper bestående av i sig oordnade polyetylenoxidkedjor.
PAPERS INCLUDED IN THE THESIS

This thesis is based on the following papers which will be referred to in the text by their roman numerals.

Johnson, C. M.; Tyrode, E.; Baldelli, S.; Rutland, M. W.; Leygraf, C.  

Tyrode, E.; Johnson, C. M.; Baldelli, S.; Leygraf, C.; Rutland, M. W.  

III. Study of the Adsorption of Sodium Dodecyl Sulfate (SDS) at the Air/Water Interface: Targeting the Sulfate Headgroup Using Vibrational Sum Frequency Spectroscopy.  
Johnson, C. M.; Tyrode, E.  

Tyrode, E.; Johnson, C. M.; Kumpulainen, A.; Rutland, M. W.; Claesson, P. M.  
*Accepted by the Journal of the American Chemical Society.*

V. Study of the Adsorption of Ammonium Perfluorononanoate at the air/water interface by Vibrational Sum Frequency Spectroscopy.  
Tyrode, E.; Johnson, C. M.; Rutland, M. W.; Bain, C. D.  
*Manuscript.*

VI. Structure and Hydration of Ethylene Oxide Surfactants at the Air / Liquid Interface: A Vibrational Sum Frequency Spectroscopy (VSFS) study.  
Tyrode, E.; Johnson, C. M.; Rutland, M. W.; Claesson, P. M.  
*Manuscript.*
PAPERS NOT INCLUDED

The following papers are also of relevance to the thesis, and are referred to in the results section.

VII. Soluble Monolayers of n-Decyl Glucopyranoside and n-Decyl Maltopyranoside. Phase Changes in the Gaseous to the Liquid-Expanded Range.

VIII. Atmospheric corrosion of zinc by organic constituents: 1. The role of the zinc/water and water/air interfaces studied by IRAS and VSFS.
Johnson, C. M.; Tyrode, E.; Leygraf, C. *Submitted.*

IX. A Vibrational Sum Frequency Spectroscopy Study of the Liquid-Gas Interface of Formic Acid-Water Mixtures.
Johnson, C. M.; Tyrode, E.; Leygraf, C. *Manuscript*

Other papers by the author:


• Allouche, J.; Tyrode, E.; Saddler, V.; Choplin, L.; Salager, J.-L., Simultaneous Conductivity and Viscosity Measurements as a Technique To Track Emulsion Inversion by the Phase-Inversion-Temperature Method. Langmuir 2004, 20, (6), 2134-2140.

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1- INTRODUCTION

A considerable number of chemical, physical, and biological processes are controlled by properties of surfaces and interfaces, which the recent surge of the nano-sciences has but emphasised. Understanding the structure of these interfaces at the molecular level represents a crucial step in furthering the knowledge in many of these fields. The number of experimental techniques available which are able to selectively probe the interfacial region, has diversified over the past decades.\(^1\),\(^2\) However, most of them are limited to solid interfaces in vacuum, while those techniques which could provide molecular information under normal pressures lack the surface sensitivity. In this sense, vibrational sum frequency spectroscopy (VSFS) has proven to be a valuable tool. Being both an optical and spectroscopic technique, it can be applied to any interface accessible by light and provide submonolayer chemical information. The surface sensitivity of VSFS resides in the second order nature of the sum frequency (SF) process, which can only occur in non-centrosymmetric media. In contrast to isotropic bulk media, at interfaces the centrosymmetry is broken, which makes it possible to distinguish just the few molecules present at the surface, even in the presence of a vast majority of the same molecules in the bulk. The key property that distinguishes molecules at an interface from those in solution is a net polar orientation.

The theoretical foundations behind VSFS were established as early as the mid sixties by Bloembergen et al.\(^3\),\(^4\) who was later awarded the Nobel Prize in Physics in 1981 for his contribution to the development of laser spectroscopy. However, it was not until the late eighties that the first vibrational sum frequency experiments were performed by Shen and coworkers.\(^5\) The first VSF spectrum of a liquid water surface and the oil/water interfaces were published a few years later.\(^6\),\(^7\) VSFS, has rapidly developed since\(^8\)\(^\text{--}^{14}\) but the complexity of the experiments and the data analysis still pose a considerable barrier to its widespread use.

In this thesis, VSFS is employed to shed some light into the hydration of different non-ionic surfactants and also the behaviour of a few selected compounds adsorbed to the air-liquid interface. VSFS is dependent on elements of both IR and Raman vibrational spectroscopies, so a brief description of the main concepts behind these techniques will be first undertaken in chapter 2. Chapter 3 deals with the general theory behind VSFS and some emphasis is made on the theoretical framework for the orientation analysis of VSF spectra. In chapter 4 a short
description of the vibrational sum frequency spectrometer as well as some details of the sample handling and preparation are presented. In chapter 5, the most important results described in the papers and manuscripts attached at the end of this thesis are briefly summarized. In the second section of this chapter a general comparison is made between the different uncharged systems studied and their influence on the water surface structure is discussed.
2- INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

Molecular spectroscopy is a branch of science where the interaction of electromagnetic radiation and matter is studied with the ultimate goal of obtaining information about molecular structure, the state of association or even the interaction with other molecules, among other properties. It is usually classified depending on the spectral range of the electromagnetic radiation used, for example microwave, infrared, visible or x-ray spectroscopies. In vibrational spectroscopy, we are concerned with vibrational transitions that lie in the infrared wavelength range (IR), though they can be also probed indirectly through the inelastic scattering of higher energy photons (Raman).

Molecular vibrations

All atoms in a molecule, which from a classical perspective can be regarded as being held together by massless springs, are constantly moving with respect to each other. Each of these motions of nuclei relative to other nuclei in the same molecule can be considered as a superposition of so called normal vibrations. Nonlinear molecules possess $3N-6$ of such normal modes, while linear molecules have $3N-5$, where $N$ is the number of atoms in the molecule. In each normal mode of vibration, all the atoms in a molecule vibrate with the same frequency and all atoms pass through their equilibrium positions simultaneously.\(^{15}\) The fundamental frequencies of the normal vibrations are dependent on the masses of the nuclei, their geometrical arrangement, the strength of the chemical bonds, and their molecular environment.

2.1- INFRARED SPECTROSCOPY

In IR spectroscopy the interaction of light and matter occurs when the energy or frequency of the incoming photon matches the frequency of one of the vibrational modes of a molecule. During this process, referred to as resonance interaction, the photon is absorbed and the molecule is promoted to a vibrational excited state. Thus, for a given sample following the changes of intensity of infrared light as a function of frequency produces an absorption spectrum, as light is absorbed at each of the characteristic vibrational frequencies. The energy range in mid IR spectroscopy usually extends from 200 to 4000 cm\(^{-1}\).
For a transition to occur, it is not only necessary for the perturbing radiation to possess the proper energy, but also the transition dipole moment must be nonzero.\(^{16}\) As a consequence, in order to absorb infrared radiation, the dipole moment of the molecule has to change during the vibration, which is an important selection rule for IR spectroscopy. This can be expressed mathematically in the following equation:

\[
\frac{\partial \mu}{\partial Q} \neq 0
\]  

[1]

where \(\mu\) is the dipole moment, and \(Q\) the normal vibrational coordinate. The intensity of an infrared band is proportional to the square of the change in dipole moment, thus \(I_{IR} \propto (\frac{\partial \mu}{\partial Q})^2\).

### 2.2- Raman Spectroscopy

Raman spectroscopy represents a different method to observe transitions between vibrational states, using photons with energies much higher than the vibrational frequencies but lower than the required to produce electronic transitions. To continue this discussion it is instructive to consider in more detail the interactions between light and matter following a classical treatment.

When electromagnetic radiation irradiates a molecule, it can react in two different ways depending on the frequency of the incident field. On the one hand, if the photon energy matches that of one of the excited states, the molecule can absorb the light (i.e. IR spectroscopy). In contrast, if the energy of the photon is far from a resonance transition, the electric field of the incident radiation induces a polarization in the molecule, which in turn acts a source, producing an electromagnetic scattered radiation through a non-resonant scattering process.\(^{17}\) Most of these reradiated photons have exactly the same frequency as those of the incident field, and the effect is known as Rayleigh or elastic scattering. However, a very small portion of the photons are scattered at different frequencies, which gives rise to the Raman effect. This effect can be regarded as an inelastic collision between the incident photon and the molecule where, as a result of the collision the vibrational energy of the
molecule, it is changed by an amount that matches one of the vibrational modes of the molecule.  

The Raman scattering process can be depicted schematically as shown in figure 1. Scattering phenomena are two photon processes, where the incident photon is momentarily absorbed into a virtual state, from where a new photon is created and scattered. The final state can either be the vibrational ground state (Rayleigh scattering) or the vibrational excited state (Stokes-Raman scattering). If the molecule is originally in a vibrational exited state, the scattering process can also proceed through the virtual state down to the ground vibrational state, producing a photon with higher energy that the incident one (anti-Stokes Raman scattering).

![Figure 1. Schematic illustration of infrared absorption, Rayleigh and Raman scattering. In IR the incident photon has the same frequency as the molecular vibration, and the molecule is exited from the ground to the first vibrational level (|g⟩ → |v⟩). In Rayleigh and Raman scattering the incident photon has much higher energy, and is first momentarily absorbed into a virtual state (dashed line), from where a new photon is scattered. In Rayleigh the scattered photon is like the incident photon, but in Raman the scattered photon has a lower or higher frequency. The difference in energy of the two photons is equal to the molecular vibrational frequency.](image)

To understand the selection rules of Raman scattering, it is instructive to describe some general considerations about the induced dipole moment, which is the origin of the scattered radiation: Within the electric dipole approximation, the induced dipole moment \( \mu_{\text{ind}} \) can be expressed in terms of the electric field, \( E \), of the incident radiation by a power series:

\[
\mu_{\text{ind}} = \alpha E + \frac{1}{2} \beta : EE + \ldots
\]  

### [2]
where $\alpha$ is the molecular polarizability, and $\beta$ the molecular hyperpolarizability. These are tensors of rank 2 and 3, with 9 and 27 elements, respectively. In most cases, and in particular for the Rayleigh and Raman scattering phenomena discussed in this section, the linear term in equation 2 is sufficient to describe the induced polarization, as it is found to have the correct frequency dependence. The implication of the second order term will be considered in a later section. In order to appreciate the full significance of the tensor character of $\alpha$, equation 2 can be rewritten in matrix form:

$$
\begin{bmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{bmatrix} = 
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
$$

It is clear from equation 3 that, for example, an electric field in the $y$ direction could induce a polarization component in the $x$ or $z$ direction. The polarizability can be visualized as the deformability of the electron cloud by the perturbing electromagnetic field, whose value varies as the molecule alternatively compresses and extends during a vibration. These changes can be expressed by expanding each component $\alpha_{ij}$ in a Taylor series with respect to the normal coordinates of a vibration:

$$
\alpha_{ij} = (\alpha_{ij})_0 + \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 Q_k + \ldots
$$

where, $(\alpha_{ij})_0$ is the equilibrium polarizability, $Q$ the normal coordinate of vibration which varies periodically, and $\frac{\partial \alpha_{ij}}{\partial Q_k}$ is the rate of change of the polarizability with respect to $Q$ for the $k^{th}$ normal mode at the equilibrium configuration. The first of these terms is responsible for the Rayleigh scattering while the second gives rise to the Raman effect. From equation 4 stems the Raman selection rule: for a vibration to be Raman active the change in the polarizability with respect to the normal coordinate must be nonzero:

$$
\left(\frac{\partial \alpha}{\partial Q}\right) \neq 0
$$
Due to their different selection rules, infrared and Raman spectroscopy, should be regarded as complementary techniques rather than alternative, in spite of both probing vibrational energy levels.

**Depolarization ratios.**

Another interesting property of Raman radiation is that it is completely or partly polarized depending on the symmetry of the vibration responsible for the scattering, even in the case of isotropic and nonoriented samples. This polarization response is normally expressed in terms of the Raman depolarization ratio ($\rho$), which relates the different elements of the Raman tensor according to equation 6 and which can be obtained experimentally.

$$\rho = \frac{3(\gamma^2)}{45(a')^2 + 4\gamma^4} \quad [6]$$

where, the mean value, $a'$, and the anisotropy, $\gamma'$, of the derived polarizability tensor are defined by:

$$a' = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad [7a]$$

$$\gamma^2 = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2) \right] \quad [7b]$$

$\rho$ is useful in the assignments of spectral features, as well as in the determination of the relative values of some hyperpolarizability elements used in the orientation analysis in vibrational sum frequency spectroscopy, as will be discussed in the next section.
3- VIBRATIONAL SUM FREQUENCY SPECTROSCOPY (VSFS)

3.1- PRINCIPLES

In general terms, VSFS is an intrinsically surface sensitive nonlinear optical technique in which two pulsed laser beams, one fixed in the visible ($\omega_{\text{vis}}$) and the other tunable in the IR ($\omega_{\text{IR}}$), are overlapped in space and time at an interface, and a third laser beam generated at the surface is detected at the sum of the frequencies (SF) of the two incident fields ($\omega_{\text{SF}} = \omega_{\text{vis}} + \omega_{\text{IR}}$). When the frequency of the infrared beam approaches one of the resonant vibrations of the species present at the surface, the SF signal is resonantly enhanced giving rise to the SF spectra.

![Schematic representation of the SF process at an interface.](image)

During the SF process, the energy and momentum of the radiation parallel to the surface are conserved, which implies that the angle of emission of the SF beam is dependent on the incident angles of the visible and IR radiations and their respective energies, as shown in the following equation:

$$\omega_{\text{SF}} \sin \xi_{\text{SF}} = \omega_{\text{vis}} \sin \xi_{\text{vis}} + \omega_{\text{IR}} \sin \xi_{\text{IR}}$$  \[8\]

where the angles $\xi_{\text{SF}}$, $\xi_{\text{vis}}$, and $\xi_{\text{IR}}$ are measured with respect to the surface normal.

In order to obtain this kind of optical response from a material, large incident fields are required which are not entirely negligible in comparison to the internal field maintaining the
electron structure in an atom. Intensities of this magnitude are obtained from pulsed laser sources.

The intensity of the sum frequency beam generated in the interfacial layer is proportional to the square of the second order nonlinear susceptibility $\chi^{(2)}$, and the intensities of the visible ($I_{\text{vis}}$) and IR ($I_{\text{IR}}$) fields,

$$I_{\text{sf}} \propto |\chi^{(2)}|^2 I_{\text{vis}} I_{\text{IR}}$$  \[9\]

$\chi^{(2)}$, which can be considered as the macroscopic equivalent to the molecular hyperpolarizability $\beta^{(2)}$ of equation 2, is also a tensor of rank 3 with 27 components (3x3x3) that relates the electric fields of the incident beams to the induced polarization at the interface. The number of independent and nonzero elements of the second order susceptibility tensor can be reduced based on symmetry considerations. According to Neumann’s principle, each of these elements taken with respect to two coordinate systems which are related by one of the symmetry operations characteristic of the medium (inversion, rotation, reflection, etc), must be identical. From this principle stems an important selection rule for VSFS. In a centrosymmetric medium, when the inversion operation is applied to $\chi^{(2)}$ a change of sign is observed for each of its elements, which implies that $\chi^{(2)}$ must vanish (equation 10). As a consequence, an SF signal cannot be generated in centrosymmetric crystals and isotropic phases, which include all gases, and most liquids and solids. At surfaces and interfaces the symmetry is broken, and $\chi^{(2)}$ is non zero, making it possible to distinguish just the few molecules present at the surface, even in the presence of a vast majority of the same molecules in the bulk.

$$\chi_{i,j,k}^{(2)} = -\chi_{-i,-j,-k}^{(2)} = -\chi_{i,j,k}^{(2)} \quad \text{which can only be true if} \quad \chi_{i,j,k}^{(2)} = 0 \quad \text{[10]}$$

This selection rule is only valid under the electric dipole approximation, since for example if electric quadrupole or magnetic dipole interactions are included in the susceptibility treatment, $\chi^{(2)}$ is non zero even for media possessing inversion symmetry, which would give rise to some bulk contribution in the SF signal. Nonetheless, these interactions can be considered negligible in most cases, and in particular for isotropic liquids which is the case of the systems studied here.
3.2- General Theory

In this section only a brief summary of the most important expressions used in the analysis and interpretation of the SF spectra is presented. A more extensive treatment of the theory can be found in other sources.\(^4\), \(^20\), \(^23\)

\[ I_{SF} = \frac{8\pi^3 \sec^2 \xi_{SF}}{c n_i(\omega_{SF}) n_i(\omega_{vis})} \left| \chi_{eff}^{(2)} \right|^2 I_{vis}I_{IR} \]  \[11\]

where \(c\) is the speed of light, \(n_i(\omega)\) the refractive index of medium \(i\) at frequency \(\omega\) (figure 3), and \(\chi_{eff}^{(2)}\) the effective nonlinear susceptibility corrected by the respective Fresnel factors:

\[ \chi_{eff}^{(2)} = \left[ \hat{e}(\omega_{SF}) \cdot L(\omega_{SF}) \right] \cdot \chi^{(2)} \left[ L(\omega_{vis}) \cdot \hat{e}(\omega_{vis}) \right] \left[ L(\omega_{IR}) \cdot \hat{e}(\omega_{IR}) \right] \]  \[12\]

where \(\hat{e}(\omega)\) is the unit polarization vector, and \(L(\omega)\) the Fresnel factor at frequency \(\omega\). For systems which are isotropic in the plane of the surface, like all the liquid surfaces studied here, the number of non zero and independent elements of \(\chi^{(2)}\) can be significantly reduced by drawing on Neumann’s principle mentioned above. Defining the laboratory coordinates with the \(x\) and \(z\) axes on the plane of incidence as shown in figure 3, the only elements of \(\chi^{(2)}\)
that remain are: $\chi_{xx} = \chi_{yy} ; \chi_{zz} = \chi_{zz} ; \chi_{xx} = \chi_{yy}$, and $\chi_{zz}$. These independent elements of $\chi^{(2)}$ can be probed using 4 different polarization combinations of the incoming and SF beams, specifically the ssp, ppp, sps, and pss polarization combinations, where the letters designate the polarization whether parallel (p) or perpendicular (s) to the plane of incidence of the SF, visible, and IR beams, respectively (i.e. ssp, “s” polarized SF, “s” polarized visible, and “p” polarized IR beam). By expanding equation 12 for the different polarization combinations the following equations are obtained:

$$\chi^{(2)}_{eff,ssp} = L_{yy}(\omega_{SF})L_{yy}(\omega_{vis})L_{zz}(\omega_{IR})\sin\xi_{IR} \chi_{yy}$$  \hspace{1cm} [13 a]$$
$$\chi^{(2)}_{eff,ppp} = L_{yy}(\omega_{SF})L_{zz}(\omega_{vis})L_{yy}(\omega_{IR})\sin\xi_{IR} \chi_{yy}$$  \hspace{1cm} [13 b]$$
$$\chi^{(2)}_{eff,sps} = L_{zz}(\omega_{SF})L_{yy}(\omega_{vis})L_{yy}(\omega_{IR})\sin\xi_{IR} \chi_{yy}$$  \hspace{1cm} [13 c]$$
$$\chi^{(2)}_{eff,pss} = -L_{zz}(\omega_{SF})L_{zz}(\omega_{vis})L_{zz}(\omega_{IR})\cos\xi_{IR} \chi_{zz} - L_{zz}(\omega_{SF})L_{zz}(\omega_{vis})L_{zz}(\omega_{IR})\cos\xi_{IR} \chi_{zz}$$  \hspace{1cm} [13 d]$$

The Fresnel factors $L_{ii}(\omega)$, which relate the fields in the interfacial layer to the fields in medium 1, depend on the angles of reflection and refraction of the respective beams, and also on the refractive indices of the media involved in the process, as shown explicitly in the following equations,

$$L_{xx}(\omega) = \frac{2n_x(\omega) \cos \gamma_j}{n_x(\omega) \cos \gamma_j + n_z(\omega) \cos \xi_j}$$  \hspace{1cm} [14 a]$$
$$L_{yy}(\omega) = \frac{2n_y(\omega) \cos \xi_j}{n_y(\omega) \cos \xi_j + n_z(\omega) \cos \gamma_j}$$  \hspace{1cm} [14 b]$$
$$L_{zz}(\omega) = \frac{2n_z(\omega) \cos \xi_j}{n_z(\omega) \cos \xi_j + n_z(\omega) \cos \xi_j} \left( \frac{n_z(\omega)}{n_z'(\omega)} \right)^2$$  \hspace{1cm} [14 c]$$

where $\gamma$ is the angle of refraction, which can be calculated using Snell's law.\textsuperscript{25} On the other hand, $n'$ represents the index of refraction of the surface layer, which is usually difficult to estimate from experimental data and constitutes a source of ambiguity when defining the theoretical models.
Reviewing equations 11 to 14, it is clear that the different nonzero susceptibility elements of the interfacial layer can in principle be experimentally determined by measuring the intensity of the sum frequency beam at the 4 different polarization combinations mentioned above, provided the optical constants of the different media are known (Fresnel factors). In order to obtain molecular and orientational information it is necessary to relate the macroscopic $\chi^{(2)}$ elements to the molecular hyperpolarizability $\beta^{(2)}$. Before doing so, it is convenient to simplify the treatment by dividing $\chi^{(2)}$ into two terms:

$$\chi^{(2)} = \chi_{NR}^{(2)} + \sum_n \chi_{R,n}^{(2)}$$  \[15\]  

The first term accounts for the non resonant contribution (NR) which encompasses the off resonant terms of the sum over states expression derived from perturbation theory. The second term includes all the $n$ resonant contributions to the nonlinear susceptibility, and can be expressed in terms of the molecular hyperpolarizability tensor in the molecular coordinate system $(a,b,c)$ as:

$$\chi_{R,n}^{(2)} = \frac{N}{\varepsilon_0} \left\langle \beta_n^{(2)} \right\rangle$$  \[16\]  

where $N$ is the number of molecules, and $\varepsilon_0$ is the dielectric permittivity. The angle brackets indicate that $\beta^{(2)}$ is orientationally averaged over all possible molecular orientations. This apparently simple equation conceals great complexity, since both $\chi^{(2)}$ and $\beta^{(2)}$ are third ranked tensors of 27 elements each, and are related through a sixth ranked tensor (729 elements) of direction cosines defined in terms of the Euler angles: $\chi$ (not to be confused with $\chi^{(2)}$), $\theta$, and $\phi$, which represent the rotation of the molecular axes $(a,b,c)$ with respect to laboratory fixed axes $(x,y,z)$. $\chi$ refers to the azimuthal angle, $\theta$ to the tilt from the surface normal, and $\phi$ to the twist angle as schematized in figure 4.

![Figure 4. Euler angle transformations ($\chi$, $\theta$, $\phi$) between molecular coordinates $(a,b,c)$ and laboratory coordinates $(x,y,z)$.](image)
Under the assumption of a two level system consisting of a ground state and a single excited state, the elements of the $\beta^{(2)}$ tensor can be related to the IR transition moment ($\mu_i$) and Raman tensor elements ($\alpha_{\alpha\beta}$), as shown in the following equation:

$$
\beta^{(2)}_{\alpha\beta\gamma} = \frac{\alpha_{\alpha\beta} \mu_\gamma}{\omega_n \omega_{\text{IR}} - i \Gamma_n}
$$

where $\omega_n$ is the vibrational transition frequency, $i$ the imaginary unit, $\Gamma_n$ the damping constant, and $\alpha\beta\gamma$ are the molecular coordinates ($\alpha = a,b,c; \beta = a,b,c$ and $\gamma = a,b,c$). When $\omega_{\text{IR}}$ is in resonance with $\omega_n$, $\beta^{(2)}$ and correspondingly $\chi^{(2)}$ are resonantly enhanced and the vibrational spectrum of the surface molecules can be obtained. From equation 17 stems an important selection rule for VSFS: a vibrational mode must be both IR and Raman active to be SF active.

### 3.3- Spectral Analysis

Analyzing the positions of the bands in a vibrational sum frequency spectrum, gives direct chemical information about the species, as well as some information about the local molecular environment (hydrogen bonded, free vibrations, etc). Only molecules with a net orientation give rise to the SF signal, since otherwise the average hyperpolarizability will be zero (equation 16). However, the lack of signal in an expected region of the spectrum could also be explained by a low Raman and/or IR transition moment (equation 17), a local centrosymmetric environment, an unfavourable orientation or simply by the absence of the molecule at the surface ($N$ in equation 16). It is usually possible to distinguish between these options, consulting for example available IR and Raman spectra from the compounds under study, or performing experiments under the different polarization combinations (ssp, ppp, and sps/pss), since some vibrational modes may be very weak or not observable in a certain polarization combination but evident in others due to symmetry and/or orientational considerations.
3.4- Orientation Analysis.

Performing experiments with different polarization combinations of the input and output fields can also be used to determine the orientation of a specific bond or group of atoms when certain input parameters are known. The procedure consists of comparing the ratios of experimentally determined amplitudes under different polarization combinations for one of the vibrational modes observed in the spectra, with theoretical curves that model the changes in the sum frequency signal as a function of orientation.

The experimental amplitudes are obtained fitting the spectra to Lorentzian lines shapes of the form presented in equation 18.

$$I_{\text{sf}}(\omega_n) = |A_{NR} + \sum_{\omega} \frac{A_n}{\omega_n - \omega - i\Gamma_n}|^2$$

where $A_{NR}$ refers to the nonresonant contribution to the SF signal, and $A_n$ to the amplitude or oscillator strength of the $n^{th}$ resonant mode, where $n$ is number of vibrational modes. For the different liquid surfaces studied in this thesis the nonresonant contribution was constrained to be a real variable, since the imaginary part of dielectric surfaces is expected to be zero far away from electronic transitions. In solid surfaces, in particular in metals like gold or silver where the nonresonant background from the substrate is as strong as the resonant contributions, $A_n$ has to be fitted as a complex variable.

The theoretical curves are calculated following a well established procedure. The first step is to identify the independent components of the hyperpolarizability tensor $\beta^{(2)}$ from considerations of molecular symmetry of the mode under consideration, which can be effectively done by referring to character tables. This approach implies approximations about the local symmetry of the functional group. For example for a symmetric vibrational mode of $C_{2v}$ symmetry, like water vibrations, the 27 elements of $\beta^{(2)}$ are reduced to only 3 independent elements: $\beta_{aac}, \beta_{abc}$, and $\beta_{ccc}$, while for the asymmetric vibrations a single independent element remains: $\beta_{aca} = \beta_{caa}$.
\( \beta^{(2)} \) is then orientationally averaged to obtain the \( \chi^{(2)} \) tensor in terms of the Euler angles (equation 16). Liquid interfaces are isotropic in the plane, thus the \( \chi^{(2)} \) expression can be integrated over the azimuthal angle (all molecular orientations around the azimuthal angle are equally likely). It can be further assumed in some cases that the twists around the principal axis of symmetry of the bond or group of atoms modelled are random, leaving a final expression of \( \chi^{(2)} \) as a function of the tilt angle (\( \theta \)) and the nonzero \( \beta^{(2)} \) elements. In the particular case of water molecules, since the twist angle (\( \phi \)) cannot be rotationally averaged, the remaining expressions for the elements of \( \chi^{(2)} \) are expressed as functions of both the tilt and the twist angle. This is demonstrated below:

For the symmetric stretching vibration: \[19 \text{ a,b,c}\]

\[
\chi_{xx,s} = \chi_{yy,s} = \chi_{zz,s} = \frac{1}{2} N \left\{ \langle \cos \theta \rangle \beta_{cc} + \beta_{bc} \langle \sin^2 \phi \rangle + \beta_{ac} \langle \cos^2 \phi \rangle - \langle \cos^3 \theta \rangle \beta_{cc} - \beta_{bc} \langle \cos^2 \phi \rangle - \beta_{ac} \langle \sin^2 \phi \rangle \right\}
\]

\[
\chi_{xx,s} = \chi_{yy,s} = \chi_{zz,s} = \frac{1}{2} N \left\{ \langle \cos \theta \rangle - \langle \cos \theta \rangle \beta_{bc} \langle \sin^2 \phi \rangle + \beta_{bc} \langle \cos^2 \phi \rangle - \beta_{cc} \right\}
\]

\[
\chi_{zz,s} = N \langle \cos \theta \rangle \beta_{bc} \langle \sin^2 \phi \rangle + \beta_{ac} \langle \cos^2 \phi \rangle + \langle \cos^3 \theta \rangle \beta_{cc} - \beta_{bc} \langle \cos^2 \phi \rangle - \beta_{ac} \langle \sin^2 \phi \rangle \right\}
\]

For the asymmetric stretching vibration: \[20 \text{ a,b,c}\]

\[
\chi_{xx,as} = \chi_{yy,as} = \chi_{zz,as} = \frac{1}{2} N \beta_{ac} \langle \sin^2 \phi \rangle \langle \cos^3 \theta \rangle - \langle \cos \theta \rangle
\]

\[
\chi_{xx,as} = \chi_{yy,as} = \chi_{zz,as} = \chi_{zy,as} = \frac{1}{2} N \beta_{ac} \langle \cos^3 \theta \rangle - \langle \sin^2 \phi \rangle \langle \cos^3 \theta \rangle - \langle \cos \theta \rangle \langle \sin^2 \phi \rangle \right\}
\]

\[
\chi_{zz,as} = -2 N \beta_{ac} \langle \sin^2 \phi \rangle \langle \cos^3 \theta \rangle - \langle \cos \theta \rangle
\]

Moreover, assuming a delta function for the distribution of twist and tilt angles the angular brackets of equation 19 and 20 can be substituted by simple parentheses. The effective nonlinear susceptibility elements for each polarization combination can be calculated through equation 13 using the Fresnel factors of equation 14. Finally the absolute intensity of the SF beam is obtained using equation 11. It is interesting to note that the values of \( I_{xys} \) and \( I_{yxs} \), and as a consequence also the spectra recorded under these two polarization combinations, only differ by a constant given by their Fresnel coefficients since \( \chi_{xyy} = \chi_{yxy} \) (equation 13) far away from electronic transition (symmetric Raman tensor).
In this way we can model the intensity of the SF beam for the different polarization combinations as a function of the orientational parameters like the tilt and twist angles. However, plotting the ratio between two different polarization combinations has the advantage of reducing the number of unknowns, like the number of molecules $N$ contributing to the signal (equation 16) and in particular the nonzero $\beta^{(2)}$ elements. For example, plotting the ratio $I_{ssp}/I_{sps}$ for the asymmetric stretching vibration of water effectively cancels the $\beta_{aca}$ and $N$ dependences from equations 20 a, and 20 b. However, when there is more than one independent $\beta^{(2)}$ element, it is necessary to refer to an external source to calculate the relative values between them. To a first approximation they can be estimated from the Raman tensor elements and IR transition dipole moments. The big challenge resides in obtaining the Raman tensor, because it is only seldom that the individual tensor elements are known. Measuring the Raman depolarization ratio (equations 6 and 7) could be useful when there are only two independent tensor elements, like for example in $C_{3v}$ symmetric vibrations, as shown below:

$$r = \frac{\beta_{aa}}{\beta_{cc}} = \frac{\alpha_{aa} \mu_a}{\alpha_{cc} \mu_c} = \frac{\alpha_{aa}}{\alpha_{cc}}$$  \hspace{1cm} [21]

where $r$ is related to the depolarization ratio by:

$$\rho = \frac{3}{4} \left(1 + 5 \left(\frac{2r + 1}{r - 1}\right)^2\right)^{-1}$$  \hspace{1cm} [22]

For more complex cases, it is necessary to rely on ab initio calculations, but the computational time required to calculate these values with sufficient accuracy for large molecules remains prohibitive. However, it is clear that ab initio calculations will become a valuable resource in the future.
4- MATERIALS AND METHODS

4.1-VIBRATIONAL SUM FREQUENCY SPECTROMETER

The installation and setting up of the instrument, including all the subsequent experimental modifications that were needed to acquire data of the quality presented in this thesis, which consumed a significant part of the first three quarters of the total PhD time, will be only briefly summarized in the following pages (additional details can be found in the experimental section of paper I36).

The KTH sum frequency spectrometer consists of 4 main parts:

- Pumping laser
- OPG/OPA (Optical Parametric Generator / Optical Parametric Amplifier)
- Sum frequency generation and detection.
- Cell and sample preparation.

- **Pumping Laser**: The laser system employed consists of an active/passive mode-locked Q-switched Nd:YAG laser (Ekspla, PL2143A/20) with a fundamental output at 1064 nm, generating pulses with a length of ~24 picoseconds, a repetition rate of 20 Hz, and an approximate energy per pulse of 40 mJ. The laser constitutes the most important element of the VSF spectrometer, since its general performance (stability and beam shape) has a direct and profound influence on the quality of the acquired spectra.

- **OPG/OPA**: The laser’s output is used to pump an optical parametric generator/amplifier (LaserVision), which generates the visible (532 nm) and tunable IR (3-12 μm) beams employed in the experiments. The energy output of the tuneable IR is frequency dependent, varying from 70 to 600 μJ/pulse in the spectral region extending from 2000 cm⁻¹ – 4000 cm⁻¹ (bandwidth of 7-9 cm⁻¹), and from 10 to 70 μJ/pulse between 850 cm⁻¹ and 1950 cm⁻¹ (bandwidth < 15 cm⁻¹). In figure 5 a schematic diagram of the OPG/OPA setup is shown. The tuneability of the IR beam is secured by angle tuned nonlinear crystals which are moved independently by stepping motors controlled by a computer interfaced with the main acquisition program.
• **Sum frequency generation and detection.** The generated tuneable IR and visible beams are directed towards the sample in a copropagating geometry, very much as shown in figure 2 and 3. The incident angles at the surface are $\beta_{\text{vis}} = 55^\circ$ and $\beta_{\text{IR}} = 63^\circ$ from the surface normal, while the SF beam angle ($\beta_{\text{SF}}$) ranged from 55.4 to 56.3$^\circ$ dependent on the IR wavelength, according to equation 8.

The polarization of the IR beam is rotated using a frequency tuneable half-wave plate (Alphalas GmbH, Germany), which is adjusted during the experiments with a stepping motor depending on the wavenumber of the IR beam. On the other hand the visible halfwave plate, and SF polarizer (Glan-Thompson) are adjusted manually between each polarization combination experiment. Approximately 95% of the IR beam path before reaching the sample is confined in a box containing an overpressure of dry air, which considerably reduces the IR losses due the absorption bands of water vapour. The beam diameters at the surface were approximately 1.5 and 1 mm for the visible and IR fields, respectively, though they were slightly varied depending on the frequency range studied.

The generated sum frequency beam is first spatially and then optically filtered by a Notch Plus filter, a band pass filter, and a monochromator before being detected with a photon multiplier tube (PMT). Gated electronics allowed discrimination of the PMT signal from the background noise. The integrated signal is acquired by a computer

*The terms wavenumber, wavelength and frequency are generally used indiscriminately to refer to the same thing, and this may be source of confusion. The wavenumber is the inverse of the wavelength, and the frequency is the wavenumber multiplied by the speed of light. Low wavenumbers, long wavelengths and low frequencies are thus equivalent expressions.*
using a Labview program. The tuning of the IR is carried out in a continuous mode with a scanning speed of 1 cm\(^{-1}\) per second.

The detected signal is normalized by the IR and visible power fluctuations, as well as by the frequency and polarization dependent properties of the optical components placed along the SF beam path (filters, monochorometer and PMT). Careful and time-consuming experiments were performed to verify the normalization procedures.

- **Cell and sample preparation.** The cleanliness of the measuring vessel was found to be of particular importance, as minute amounts of contaminants are sufficient to foul the liquid surface. The main features of the measuring cell for liquid / air interfaces can be appreciated in figure 6. The main body is made out of glass while the hollow stoppers are machined in Teflon, and accommodate IR transparent CaF\(_2\) or BaF\(_2\) windows which are exchanged depending on the frequency range studied. The two smaller upper arms are used for IR normalization, where a portion of the main IR beam is passed through to account for IR power fluctuations and gas-phase absorption. An advantage of this design is that it allows experiments at different concentrations that require the addition of a certain amount of liquid to be carried out continuously, since the increase in the liquid volume in the cell can be compensated by the vertical displacement of the cell setup, without having to make any changes in the optical alignment.

![Figure 6. Schematic of the sample cell used for VSFS experiments. The visible and IR beam reflections from the liquid surface are omitted for clarity.](image)
It is worth noting here the importance of performing the experiments in a closed cell, not only for the correction of the absorption of the IR beam before reaching the sample’s surface, but in particular to avoid contamination of the high energy surface of pure water by airborne contaminants. An illustration of this effect is shown in figure 7a and 7b. Both graphs show the fluctuations of the SF signal for the “free OH” peak at 3702 cm$^{-1}$ from the surface of pure water, as a function of time in a cell open to the laboratory air. The evident drop in the intensity measured is a consequence of the adsorption of contaminants from the surrounding air, while the scattering in the experimental data is explained in terms of contaminants moving in and out of the probing area. Considerably higher signal losses are obtained under humid conditions (figure 7b). When performing similar measurements in the closed cell depicted above, the signal was seen to remain constant even after more than 48 hours of experiments. When considering that on average four hours were needed to collect spectra in the OH vibration region of water, it becomes clear that a closed cell is not only desirable but also necessary.

![Figure 7](image-url)

**Figure 7.** Variation of the water surface SF intensity at 3702 cm$^{-1}$ of the free OH in the ssp polarization combination as a function of time, in a cell open to the laboratory air. A) Under relatively dry conditions: relative humidity (RH) between 25-35%. B) Under more humid conditions during one of the short Swedish summers (RH 80-90%).

The bottom of the measuring cell is immersed in a temperature controlled bath, while the temperature inside the cell is monitored with a thermocouple placed inside a glass capillary sealed on one side, which is in direct contact with the measuring liquid.
4.2- SURFACE TENSION MEASUREMENTS

In many of the papers discussed in this thesis, surface tension measurements were carried out as an independent method to estimate the number of molecules (N) contributing to the SF signal, the relevance of which can be fully grasped by examining equation 16. The surface tension isotherms were obtained using the Wilhelmy plate method, which essentially measures the change in weight of a plate brought into contact with a liquid.\textsuperscript{37} The surface tension of surfactant systems decreases with concentration until the critical micellar concentration (cmc) is reached, above which it is seen to remain practically constant. The adsorbed amount is calculated using the Gibbs equation and equimolecular dividing surface, which for non-ionic surfactants with no changes in the activity factor, can be expressed as:

$$\frac{d\gamma}{d \ln c} = -RT \Gamma$$ \hspace{1cm} [23]

where $\gamma$ is the surface tension, $c$ the surfactant molar concentration in the bulk liquid, $R$ the gas constant, $T$ the temperature, and $\Gamma$ the adsorbed amount. The area per molecule at the interface is related to the adsorbed amount through the relation $A=1/\Gamma N_AV$, where $N_AV$ is Avogadro’s Number and $A$ the area per molecule.
4.3-MATERIALS

The molecular structures of most of the surfactants studied in this work are shown in Figure 8. Short chain molecules were also investigated as model compounds, relevant for both surface chemistry and corrosion science. The purity of the substances used was of extreme importance, and great care was taken with their purification. A clear example of this problem is illustrated by initial studies performed with mixtures of water and acetic acid with a claimed purity of 99.9%. Under certain concentrations strong peaks characteristic of long chain hydrocarbons appeared in our spectra. It was concluded that the contaminant was most probably a plasticizer that leached out from the plastic container, at concentrations undetectable for the majority of bulk studies. Surfactant systems were in most cases purified by recrystallization and/or by making use of the surfactant purification unit,\(^{38}\) in particular when working below the respective cmcs. On the other hand, the shorter chain molecules, which were exclusively purchased in glass containers, were triply distilled. Partially deuterated compounds were also used to elucidate some the spectral assignments.

![Figure 8. Molecular structures of the surfactants studied in this thesis. The x in the C\(_{12}\)E\(_x\) case was either 4, 5 or 8. SDS and APFN stand for sodium dodecyl sulphate and ammonium perfluorononanoate.](image-url)
5- RESULTS AND DISCUSSION

5.1- WATER

Water, in spite of being the most ubiquitous of all liquids, still remains poorly understood. Its apparent simplicity, consisting of 2 single hydrogen atoms attached to an oxygen atom, conceals a vast complexity with unique capabilities and unusual properties.39 The key to understanding the properties of liquid water is to understand its local structure and dynamics. Due to the development of new techniques, recent years have seen a large increase in our understanding of the structure and dynamics of liquid water and as a result some “established facts” have been challenged.40, 41 It has commonly been accepted that the liquid water structure is characterized by a broken network of essentially tetrahedrally coordinated water molecules.42 Thus, the results of Wernet et al.,41 obtained by employing near edge fine structure X-ray absorption spectroscopy in combination with ab initio calculations performed by Kuo et al.,43 which indicated that around 80% of the molecules in liquid water only form two strong hydrogen bonds (one donor and one acceptor bond), and in addition two weaker hydrogen bonds, have spurred considerable interest and debate. If the results of Wernet et al. stand the test of time, the implication is that water molecules in the liquid state preferentially form chains and rings rather than a tetrahedral network.

A range of techniques can provide valuable information on the structure and dynamics of bulk liquid water. The choice for the experimentalists who need to develop understanding for the structure of the water surface region is significantly more limited, and here vibrational sum frequency spectroscopy is indeed a valuable tool.11, 44

The SF spectra of pure water using the ssp, ppp, and sps polarization combinations in the OH stretching region are shown in Figure 9. As discussed above, each of the different polarization combinations probe different components of χ(2) (equation 13) and give complementary information about the surface species and their orientation. The vibrational spectrum in this region is of particular interest because the OH stretching modes are known to be very sensitive to the number and strength of hydrogen bonds, red shifting more than 600 cm\(^{-1}\) when going from isolated water molecules in the gas phase to tetrahedrally coordinated hydrogen bonded water molecules in ice. Examining the ssp spectrum, two main features can readily be
distinguished: a broad band extending from below 2800 up to ~3600 cm\(^{-1}\) and a sharp and strong peak centred at 3705 cm\(^{-1}\). As mentioned before, spectral features at high frequencies are indicative of water molecules vibrating with no or very weak interactions with neighbouring molecules. In this sense the peak at 3705 cm\(^{-1}\), which is characteristic of VSF water spectra, is assigned to the stretching vibrations of water molecules with an OH bond protruding out in the gas phase and vibrating free from hydrogen bonds.\(^6,\)\(^7\) Only molecules present at the top monolayer can be responsible of this intensity, a fact which demonstrates the surface sensitivity of VSFS.

**Figure 9.** Vibrational sum frequency spectra of pure water at the liquid/vapour interface. Spectra collected under the polarization combinations ssp, sps, and ppp at 20°C.

The broad band corresponds to OH stretching vibrations of water molecules present in the first two monolayers\(^45\) and participating in hydrogen bonding with other neighbouring molecules. The lower the frequency (lower wavenumbers), the greater the strength and coordination of the hydrogen bonds. The detailed assignment of the water species contributing to this band is still a source of debate, but the simplest approach has been to separate the band into two broad peaks\(^6,\)\(^11,\)\(^12\) centred at ~3200 cm\(^{-1}\) and at ~3450 cm\(^{-1}\), loosely referred to as “ice like” and “liquid like”. The former one is close in frequency to the OH
stretching mode of tetrahedrally coordinated water molecules at the surface of ice\textsuperscript{46} (~3150 cm\textsuperscript{-1}). In contrast, the weaker hydrogen bonded peak at higher frequencies, is associated with molecules vibrating in a more disordered hydrogen bonded network, in analogy to the strongest feature observed in the Raman spectrum of liquid water.\textsuperscript{47}

In the ppp polarization combination the sharp peak at 3705 cm\textsuperscript{-1} is assigned, similarly to the ssp spectrum, to the dangling or free OH vibration. On the other hand, no SF intensity is observed in the hydrogen bonded region, besides a weak feature centered at ~3500 cm\textsuperscript{-1}, which due to its relative high frequency is assigned to OH bonds only weakly perturbed by hydrogen bonding to neighbours. Moreover, in the sps spectrum no evident resonant features are observed in the entire OH stretching range.

The data at different polarization combinations allows calculation of for example, the average tilt of the OH bond that protrudes out into the vapor phase (35° from the surface normal\textsuperscript{6, 33}), but it also provides additional information about the nature of the different species responsible for a certain spectral feature. The fact that almost no intensity is observed in the spectral region below 3500 cm\textsuperscript{-1} in the ppp and sps spectra, indicates that the intensity in this region observed in the ssp spectrum essentially originates from symmetric stretching vibrations of water and/or hydrogen bonded uncoupled OH vibrations (paper IV),\textsuperscript{48} a statement which is in accordance with recent theoretical calculations.\textsuperscript{45, 49}

![Figure 10. Lateral view of an ideal basal surface of ice I\textsubscript{h}. Note the (3D) tetrahedral arrangement of the water molecules.](image)

The VSF spectra presented in figure 9 reveals that the structure of liquid water at the surface is particularly ordered. This structure has been referred to as ice-like,\textsuperscript{9, 50} although it is certainly not as ordered as ice, as evidenced by the significant intensity at ~3450 cm\textsuperscript{-1} in the
Vibrational Sum Frequency Spectroscopy Studies at the Air - Liquid Interface

ssp spectrum. In figure 10, a lateral view of a basal surface of hexagonal ice (I_h) is shown for reference. I_h is the ordinary form in which snow and ice are found on Earth at normal pressures. The ideal structure presented in figure 11 is expected to be found at the surface of ice, provided the temperature is sufficiently low (<200 K) to avoid the formation of a quasi-liquid layer.\textsuperscript{51} Note that all water molecules are arranged in a tetrahedral hydrogen bonded network and that the free OH bonds are perpendicular to the surface. In contrast, the dangling bonds in liquid water are tilted on average by ~35° from the surface normal. To minimize the surface energy, the water molecules will tend to retain as many hydrogen bonds as possible, and in the basal ice I_h surface this is accomplished by sacrificing one out of the four tetrahedral bonds per molecule residing at the surface. In the surface of liquid water the tetrahedral network is not complete and the surface structure is more disordered. Nonetheless, careful VSF experimental studies at ice interfaces have suggested that the liquid water surface, which is structurally different from the quasi-liquid layer normally found on ice surfaces, exhibits a higher degree of order than that observed at the ice surface close to the melting point.\textsuperscript{46}

5.2- EFFECT OF ADSORBATES IN THE WATER SURFACE STRUCTURE

Upon addition of a surface active compound, the surface water structure is seen to be quickly perturbed. However, with the current instrument limitations, surface densities of at least 700 – 400 Å\textsuperscript{2} per molecule are generally required to observe a change in the spectra of pure water, which makes VSFS somehow less sensitive than carefully performed surface tension or ellipsometric measurements.

In figure 11, the VSF spectra aqueous solutions of acetic and formic acid under the ssp polarization combination are shown. At these low selected concentrations it is noteworthy how the bonded OH region extending from 3000 - 3500 cm\textsuperscript{-1} and the free OH peak at ~3700 cm\textsuperscript{-1} have significantly decreased in intensity, as well as the appearance of the CH stretching vibration of formic acid at 2925 cm\textsuperscript{-1} and the methyl symmetric stretch at 2945 cm\textsuperscript{-1} for acetic acid. As discussed in papers II, IV, and VI, the presence of the sharp free OH peak is indicative of patches of unperturbed water at the surface. Moreover, it is also argued that the sharp free OH intensity is the result of the structuring and cooperative interactions of a certain number of water molecules in the surrounding liquid, and not due to single isolated
molecules. When solute molecules are adsorbed these domains are perturbed and the intensity of the free OH peak as well as the bonded OH band from water molecules supporting this structure, are expected to decrease. This is the case of the spectra presented in figure 11. Nonetheless, it is also important to consider that as the concentration of the surface active component increases at the surface, OH bands originating from direct interactions between the adsorbate and water molecules or from the adsorbate itself, will start appearing in the OH stretching range and may complicate a direct correlation between the bonded OH band and the free OH peak. For example in both spectra of figure 11, two broad bands centred at $\sim 2975$ cm$^{-1}$ and $\sim 3620$ cm$^{-1}$, which become more evident at higher concentrations, slightly overlap the original water bands from the neat surface. These bands are characteristic of the acids and their interactions with water. They are ascribed to OH stretching vibrations of hydrogen bonded acid (formic and acetic), and to ordered water molecules weakly interacting with neighbours, respectively. Another interesting example to consider is the case of charged species at the surface, where the electrostatic surface field is known to induce an enhanced ordering of the interfacial water molecules. This enhanced ordering is reflected in an increase in the intensity of the bonded OH bands, which overlap with those of pure water.

![Figure 11. VSF spectra of aqueous solutions of formic and acetic acid at 4°C, taken under the ssp polarization combination. Note the presence of the sharp free OH peak at 3700 cm$^{-1}$ in both spectra.](image)

The sharp free OH peak in aqueous solutions of acetic acid is seen to disappear from the spectra at bulk molar concentrations of $\sim 1.5\%$, which correspond to areas per molecule close to 90 Å$^2$ (at this adsorption stage the surface tension still decreases linearly with concentration which is indicative of the absence of interaction in the surface). Taking into account that the
actual area of an acetic acid molecule with its methyl group aligned perpendicular to the
surface plane is approximately 24 Å², evidences that the free OH configuration must
necessarily involve a certain number of neighbouring water molecules, and as soon as these
domains are significantly disturbed the sharp free OH peak disappears. Similar arguments
can be raised for the formic acid case.

In figure 12, the VSF spectra of dilute aqueous solutions of two non-ionic surfactants are
shown for concentrations significantly below their cmc (2200 μM for C10 Maltoside and 71
μM for C12E5), which correspond to the concentration regime between the Henry range and
the liquid expanded phase⁵⁵ (paper VI). The presence of the free OH peak in both spectra
indicates that patches of unperturbed water are indeed present at the surface. As for the formic
and acetic acid spectra, the bonded OH band in the sugar based surfactant spectra, is seen to
be correlated with the free OH peak, both decreasing simultaneously. In contrast, the C₁₂E₅
spectra show a different behaviour. This peculiarity in the ethylene-oxide (EO) based
surfactants is explained in terms of the structuring effect induced on the water surface by the
EO chains (paper VI). The intensity observed in the bonded region in the C₁₂E₅ spectra is
consequently envisioned to originate from the hydrogen bonded water molecules supporting
the free OH configuration and also from those forming the structured hydrating layer around
the surfactant headgroup.

Figure 12. VSF spectra of C10 Maltoside and C12E5 aqueous solutions, collected under the ssp polarization
combination. The ssp spectrum of water is also included for reference.
In these surfactant systems the sharp free OH peak is seen to disappear from the spectra at molecular areas of approximately 80 Å² and 65 Å² for the C10 Maltoside and C₁₂E₅, respectively. In contrast to the small acid molecules shown in figure 12, the surfactant molecules strongly interact with each other and in the literature surface micelles have been proposed to exist at these relatively low surface densities.⁵⁵-⁵⁷ These effects must be considered when estimating the size of the domains associated with the dangling OH. Moreover, the smaller molecular areas reached in the ethylene oxide case could also be related to the structure making properties of the EO chains, which might stabilize rather than perturb the free water domains.

5.3- ACETIC ACID AND WATER MIXTURES

Acetic acid / water mixtures provided a good starting point for the fundamental exploration of the formation of Gibbs monolayers at the water-gas interface, and also represented a model system to explore the full capabilities of the VSFS technique. Acetic acid is fully miscible with water and shows an interesting concentration dependent interfacial behaviour. VSFS spectra were gathered in the whole concentration range (0-100%) under the polarization combinations ssp, ppp, and sps, specifically targeting the CH, OH, C=O, and C-O stretching vibrations, which allowed a thorough study of the surface of aqueous acetic acid solutions to be made, including a detailed orientation analysis. In figure 13, spectra of the neat acetic acid and a few selected concentrations of its mixtures with water are shown. In this spectral range, the strongest feature observed is the symmetric methyl stretch, νₛ(CH₃), at 2946 cm⁻¹. The structure of the water surface becomes disrupted even at very small additions of acetic acid.

Experiments with deuterated acetic acid and heavy water were also performed to clarify some assignments, in particular the OH-stretch of hydrogen-bonded acetic acid centred at ~2975 cm⁻¹. In figure 14, the spectrum of the C=O stretch for a 7% acetic acid solution taken under the polarization combinations ssp, ppp, sps, and pss is displayed. Far from electronic transitions, the χ(2) elements probed by the last two polarization combinations are equal and the spectra therefore only differ by the Fresnel factor. For the experimental geometry used these factors are almost identical, a fact that is reflected in the spectra. The C=O band displays a peculiar concentration dependence, first increasing at low acetic concentrations and then decreasing at concentrations above 7 % acetic acid. For concentrations higher than 43%, the
C=O peak is not detected. One argument to explain this behaviour could be an increased disorder of the acetic molecules at higher concentrations. However, a careful orientation analysis provided proof for the opposite argument: an extended organization of the surface layer, with the preferential formation of cyclic dimers.

Figure 13. VSF spectra of aqueous solutions of acetic acid at 4°C. All spectra shown were taken under the ssp polarization combination. The ssp spectrum of water is also included for reference.

Figure 14. VSF spectra of ν(C=O) at 7% acid in four different polarization combinations: ssp, sps, pss, and ppp.

The orientation of the methyl and carbonyl groups of the acetic acid molecule were found, within experimental error, to remain constant throughout the whole concentration range. The two tilt angles calculated from the orientation analysis (θ_C=O and θ_CH3) are shown in the sketches in figure 15. The narrow distributions of angles allowed constraining the possible
orientations of the whole molecule at the surface to a rather small window. The acetic acid molecule remained in a basically upright position throughout the entire concentration range. The dominant acetic acid species at low bulk concentration is the hydrated monomer ($M_h$), whereas the presence of the cyclic dimer species was inferred from the data, first appearing at concentrations slightly lower than 7% and essentially saturating the surface close to 50% bulk acid concentration.

Figure 15. Sketches of the carbonyl (a) and methyl (b) orientation with respect to the surface normal. The angles shown were calculated under the assumption of a $\delta$ distribution of angles.

A sketch of the proposed surface structure of aqueous acetic acid solutions at different concentrations regimes is shown in figure 16. Very recent VSFS measurements have suggested the formation of similar antiparallel double layer structures for the neat methanol\textsuperscript{58} and acetone\textsuperscript{59, 60} surfaces.

Figure 16. Sketch of the proposed surface structure at different concentrations. Black, grey and white spheres represent carbon, oxygen and hydrogen atoms, respectively.
5.4- Non-Ionic Surfactant Systems

The adsorption behaviour and hydration structure of ethylene-oxide and sugar based non-ionic surfactants was systematically studied using vibrational sum frequency spectroscopy. In paper VI the changes in the surface structure of water in response to the formation of a liquid expanded monolayer of penta(ethylene oxide) n-dodecyl ether (C$_{12}$E$_{5}$) are explored. In figure 17, the adsorption isotherm for C$_{12}$E$_{5}$ at 20°C is shown for reference. In the 2D gas phase or Henry concentration range (< 0.1 μM), no differences were observed in the measured spectra from those of pure water under the ppp and ssp polarization combinations. It is not until the end of the Henry range when the molecular areas are close to 400 Å$^2$, that measurable changes are detected in all spectra.

From very low concentrations the EO chain of C$_{12}$E$_{5}$ induces a structuring effect at the water surface (figure 12), especially when compared with the other uncharged adsorbates. In the concentration range extending from 0.1 μM to ~ 1 μM, the main spectral features observed in the CH stretching region correspond to methylene stretching vibrations, while the resonant features related to the methyl group, in particular the asymmetric stretching vibration at 2960 cm$^{-1}$ are essentially absent from the spectra. At concentrations higher than 1 μM, which correspond to areas per molecule lower than 65 Å$^2$, the methyl vibrations become evident as shown in the spectra of figure 18.

The surfactant molecules are then inferred to lie on the surface with their hydrocarbon tails close to the surface plane for concentrations below 1 μM. In the surface density range
extending from 400 Å² to 65 Å² the sharp “free OH” peak in the spectra indicates that patches of unperturbed surface water are present on the surface. The observed results are consistent with the formation of disk-like “surface micelles” with a flat orientation of the amphiphiles at low surface concentrations, which have been proposed,⁵⁶, ⁵⁷ and thoroughly accounted for in the literature.⁵⁵ The disappearance of the free OH peak at ~65 Å² coincides with a rapid change in the orientation of surfactant tails, which adopt a more upright configuration as the surface covering liquid expanded layer is formed. Increasing the concentration also promotes a reduction in the number of gauche defects in the monolayer. However, a significant number of gauche defects remain even above the cmc. Gauche defects in the hydrocarbon monolayer are inferred by the presence of the methylene modes in the spectra, since if the hydrocarbon chains were in an all-trans configuration the methylene groups would lie in a locally centrosymmetric environment, effectively rendering the CH₂ vibrations SF inactive.⁶¹

Noteably, experiments performed on the C-O-C stretching region in conjunction with spectra taken for an isotope of C₁₂E₅ having a perdeuterated alkyl chain shown in figure 19, where essentially no resonant features were detected, lend support to the conclusion that most of the headgroup is essentially randomly oriented with probably only the first EO segment attached to the alkyl chain displaying some preferred orientation. The results obtained indicate that while the EO headgroup has no preferred orientation, the water molecules surrounding this polar group are in fact significantly oriented. In contrast sugar based surfactants seem to show the opposite behavior. Spectra taken with alkyl maltoside with perdeuterated chain, reveal that the sugar headgroups have a preferred orientation along the whole concentration range up to
the cmc, while ordered water molecules hydrating the headgroup are only observed at concentrations close to the cmc.\textsuperscript{62}

![Graph showing VSF spectra of 130 μM solution of d-C\textsubscript{12}E\textsubscript{5} under the polarization combinations ssp, ppp, and sps at 10°C and 30°C. The ssp and ppp spectra have been offset for clarity by 3 and 6 a.u. respectively.]

**Figure 19.** VSF spectra of 130 μM solution of d-C\textsubscript{12}E\textsubscript{5} under the polarization combinations ssp, ppp, and sps at 10°C and 30°C. The ssp and ppp spectra have been offset for clarity by 3 and 6 a.u. respectively.

Ethylene-oxide based surfactants and polymers have the unusual property that they phase separate when temperature is increased. In the literature, three different mechanisms have been proposed to rationalize this anomalous behaviour.\textsuperscript{63} In the conformational model, the peculiar behaviour of EO chains is attributed to a change in their conformation with temperature.\textsuperscript{64} At low temperatures the preferred conformation around the C-C bonds are of a gauche type, while at high temperatures the trans conformation is favoured. The other two models explain the clouding phenomena from the water perspective. However, they fundamentally differ in the origin of this behaviour. The first of these models\textsuperscript{65, 66} (Kjellander’s model), proposes that the hydration of the PEO chain is similar to the one observed for non polar solutes, where they are surrounded by a water clathrate structure with the added advantage that they can form hydrogen bonds with the ether oxygens. The solubility at low temperatures is explained by a fine balance between the enthalpy and entropy term. As temperature is increased the entropy term augments faster and the PEO chains associate. In this model, it is the actual hydration that drives the phase separation. The second model, is based on a hydrogen bond mechanism and it is proposed that the surfactant head group simply becomes dehydrated at elevated temperatures.\textsuperscript{67-70} The water molecules in this model are not described to form any particular structure around the PEO chains.
Experiments at different temperatures show no indication of a change in orientation of the headgroup, as proposed by the conformational model. On the other hand, the ordered structure observed around the poly(ethylene oxide) headgroups and the small disordering of this hydrating structure at higher temperatures, support the model presented by Kjellander.

5.5- NON-DONOR WATER BAND.

At relatively high frequencies (~3580 cm\(^{-1}\)) in the OH stretching range of the sps and ppp spectra, a common band to all non-ionic surfactant studied (sugar-based, ethylene oxide based and even in fatty alcohols) was observed. In figure 20 the spectra for C10Maltoside and C\(_{12}\)E\(_4\) at concentrations above cmc are shown. This band is absent in the pure water spectra and therefore the water species responsible for this intensity must be due to the presence of the surfactant, while its high frequency is indicative of water molecules only weakly interacting with neighbours. Actually in bulk Raman studies\(^\text{47, 71, 72}\) it is generally agreed to consider intensity components above 3500 cm\(^{-1}\) as non-hydrogen bonded, though it is important to make the distinction with the uncoupled free OH vibrations observed at higher frequencies in both the vapor/water and oil/water\(^\text{73}\) interfaces.

![Figure 20](image_url)

Figure 20. VSF spectra for the polarization combinations sps, ppp and sps of an aqueous solution of 0.15 mM solution of C\(_{12}\)E\(_4\) at 20\(^\circ\)C (left figure) and of C\(_{10}\)Maltoside at a concentration of 2.6 mM and 22 \(^\circ\)C (right figure). The “free OH” peak of pure water under ssp polarization combination is also shown for reference. The lines are guides to the eye.

This band was assigned to water molecules vibrating in close proximity to the hydrocarbon tails and very weakly interacting with neighbouring H\(_2\)O molecules in a “non donor” configuration. The fact that the signal intensity was significantly higher in the sps and ppp
than in the ssp polarization combination spectra, was used to obtain more information about the nature of this water species, performing an orientation analysis. In figure 21 the theoretical curves for the polarization intensity ratios ssp/ppp, ssp/sps, and sps/ppp are shown as a function of the tilt ($\theta$) and specific twist ($\phi$) angles, where a delta distribution for both $\theta$ and $\phi$ were assumed (details in paper IV). Since the experimental ratios $I_{ssp}/I_{ppp}$ and $I_{ssp}/I_{sps}$ for this band are always $< 1$, it can be seen in figure 21 that this condition can only be met for water molecules having $C_{2v}$ symmetry with an asymmetric character, since for $C_{2v}$ symmetric and $C_{\infty v}$ cases the experimental ratios do not, in most occasions, even intersect any of the theoretical curves.

The range of possible angles for the twist and tilt despite being broad, was seen to be consistent with both hydrogen atoms preferentially oriented toward the hydrocarbon tails and not forming hydrogen bonds. Moreover, interference between the free OH band and the 3580 cm$^{-1}$ band observed in the ppp and sps spectra in the concentration dependent series (paper
Results and Discussion

VI), indicate that both bands have the same phase, adding support to the “non donor” assignment.

The reason for the “non donor” orientation to be favoured over the uncoupled “free” orientation for nonionic surfactant monolayers at the water-air interface is not entirely obvious and we can only speculate about its origin. Clearly, the main difference to the case of a hydrocarbon–water interface is the presence of hydrophilic groups which alternate with hydrophobic patches from the tail region over short distances. Thus these results suggest as mentioned before, that the free OH configuration is the result of a structured layer at the interface, involving a certain number of neighbouring water molecules. When these domains are perturbed by the polar headgroups, the structuring is lost or significantly disturbed, and the preferred orientation of the “non donor” molecules is seen to arise, probably due to weak interactions between the hydrocarbon tails and water.

5.6- SODIUM DODECYL SULPHATE

VSFS was also used to study the adsorption behaviour of sodium dodecyl sulphate (SDS) to the liquid/vapour interface of aqueous solutions, specifically targeting the sulphate headgroup stretches. The range of frequencies studied spanned from 980-1850 cm\(^{-1}\). Very few experiments have been performed in this region because the energy generated in the OPG/OPA is significantly lower at these wavenumbers compared to the CH/OH range. In figure 22, spectra under the polarization combinations ssp, ppp, and sps for a SDS solution above the cmc is presented.

Probably the most striking feature in figure 22 is actually the few peaks that appear in the spectra. Several peaks originating from SO\(_3\) vibrations, C-C stretches, and hydrocarbon deformation modes in the 980-1850 cm\(^{-1}\) region are visible in Raman and IR spectra. However, many of these modes will not be SF active, since they either are IR or Raman inactive. The modes observed are the symmetric SO\(_3\) stretching vibration, \(v_s(\text{SO}_3)\), at 1070 cm\(^{-1}\) in the ssp and ppp spectra, and an anti-symmetric stretching mode, \(v_a(\text{SO}_3)\), at 1225 cm\(^{-1}\) in the sps spectrum.
Figure 22. SF spectra of a 37 mM SDS solution acquired under the ssp, ppp, and sps polarization combinations. The ppp and ssp spectra have been offset for clarity by 5 and 10 arbitrary units (a.u.) respectively. The magnified sps spectrum is shown in the inset.

The relative amplitudes of the peaks in these spectra reveal that the headgroup has a constant orientation with the pseudo-C₃ axis close to the surface normal in the whole concentration range studied (1.0 mM to well above the cmc at 8.1 mM) as later confirmed by other authors. These conclusions are further substantiated by a comparison of the fitted amplitudes of $\nu_s$(SO₃) with surface tension data, revealing that the concentration dependent amplitudes perfectly agree with the scaled surface densities acquired from fitting the surface tension data. This is shown in figure 23. Moreover, the headgroup orientation is determined to be independent on the concentration of NaCl in the range 0-300 mM.

Figure 23. Fitted amplitudes for the symmetric SO₃ stretching vibration ($A_{\nu_s}$(SO₃)) as a function of SDS concentration for the ssp and ppp polarization combinations. The grey and black curves overlapping the data points at concentrations below the cmc are the normalized adsorption isotherm obtained from fitting surface tension data. Sketches of the sulphate headgroup and the the SDS surfactant molecule are shown on the right.
Finally, it is worth noting that while some previous infrared external reflection spectroscopy (IERS) studies suggest a significant increase in the conformational order of the alkyl SDS chain with increasing surfactant concentration, this is not reflected in the headgroup orientation, which is apparently highly insensitive to both the ionic strength and monolayer density.

5.7- FLUOROCARBON SURFACTANTS

Fluorocarbon chains are bulkier (cross-sectional areas of ~30 Å² vs ~20 Å²), stiffer (trans/gauche interchange energy barrier of 4.6 vs 2.0 kJ mol⁻¹), and more hydrophobic (one CF₂ unit is equivalent to ~1.7 CH₂ units) than their hydrocarbon counterparts. Moreover, in contrast to their strong intramolecular bonds they display low cohesive energies, largely as a result of their low polarizabilities, which is reflected in their corresponding lower surface tensions and higher vapour pressures.

The adsorption behaviour of ammonium perfluorononanoate (APFN) at the air-liquid interface was studied using VSFS, specifically targeting the CF and carboxylate stretches. In figure 24 the VSF spectra of 11.6 mM APFN solution under the polarization combinations ssp, ppp, and sps are presented. The spectra correspond to a surfactant monolayer at a concentration above the critical micellar concentration (8.9 mM). As for sodium dodecyl sulphate, one of the most striking feature in the spectra is their simplicity, in particular when compared with IR and Raman spectra for the same compound. For a particular vibrational mode to be SF active, it must be both IR and Raman active, though resonant features may also be absent from the SF spectra due to orientational or conformational reasons.

For the ssp and ppp polarization combinations shown in figure 24, the main features are two strong overlapping peaks centred at 1369 and 1408 cm⁻¹, assigned to CF₃ and symmetric carboxylate stretches, respectively. The strongest peak in the sps spectrum at ~1665 cm⁻¹ is assigned to the asymmetric carboxylate stretch. The proximity in frequency of the fluorocarbon and carboxylate stretching vibrations allowed extracting information about the orientation of the surfactant headgroup and the fluorocarbon tail. The assignment of the 1369 cm⁻¹ is not straightforward, and a number of additional experiments with partly fluorinated surfactant molecules were required to unequivocally correlate it with the CF₃ group. The
proposed assignment is in disagreement with a frequently referred assignment in the literature to interpret infrared reflection/absorption spectra of self assembled monolayers. These results demonstrated the potential of VSFS to dispel doubts in the assignment of certain peaks, independently from IR and Raman experiments.

Figure 24. SF spectra for a 11.6 mM APFN solution acquired under the ssp, ppp, and sps polarization combinations. The ppp and ssp spectra have been offset for clarity by 40 and 80 arbitrary units (a.u.), respectively. The magnified sps spectrum is shown in the inset.

VSF spectra were gathered from 1 mM to above the critical micellar concentration. The fitted amplitudes for the CF₃ and the symmetric COO⁻ peaks are shown in figure 25 (left). In this figure the fitted amplitudes are seen to rapidly increase at low concentrations, reaching an almost constant value at approximately 4 mM, which is well below the cmc (8.9 mM). Normalizing the fitted amplitudes by the number density obtained from previous neutron reflection measurements allowed to disentangle the effects of number density and orientation information in the SF spectra measured. The results suggest that the orientation of both the carboxylate headgroup and CF₃ group from the fluorocarbon tail remain constant in the concentration range extending from ~1 mM to above cmc. The approximately constant ratio between the ssp and ppp fitted amplitudes also confirmed this tendency as shown in figure 25 (right).

The actual orientation of the carboxylate group was obtained performing an orientation analysis of the COO⁻ stretches. The orientation of the carboxylate group was found to remain constant with its C₂ axis very close to surface normal (< 5° tilt) from concentrations above the
cmc down to approximately 1 mM, which correspond to areas of ~65 Å² per surfactant molecule. Below 1 mM the tilt of the carboxylate group was seen to suddenly increase.

Figure 25. Left: Fitted amplitudes of the COO⁻ symmetric stretching ($A_{\nu(COO^-)}$) and the “CF₃” stretching vibration ($A_{\nu(CF_3)}$), as a function of APFN concentration for the ssp and ppp polarization combinations. Right: Ratio of the fitted amplitudes ($A_{ssp}/A_{ppp}$) of $\nu$ (COO⁻) and $\nu$ (CF₃) vibrations for APFN solutions at different concentrations.

On the other hand, though constant, the actual orientation of the fluorocarbon chain could not be determined due to limitations defining the theoretical model. Nonetheless, the absence of spectral features characteristic of CF₂ stretching vibrations, and the previous external reflection Fourier transform infrared spectroscopy (ER-FTIRS) measurements performed on the same monolayer,⁸³ provide complementary information allowing to infer that the fluorocarbon chain is significantly tilted from the surface normal in a configuration free from gauche defects.

In comparison to hydrocarbon surfactants, the orientation of the fluorocarbon chain seems to be particularly insensitive to changes in the area per molecule. This difference was explained by the higher stiffness of the perfluorinated chain.
6- CONCLUDING REMARKS

The results presented in this thesis have demonstrated the unique capabilities of vibrational sum frequency spectroscopy to explore the structure of liquid-air interfaces. One of the major contributions of this work has been the new insight given into the structure of water at the liquid surface and how it is affected by the presence of polar adsorbates. In particular, the structuring effect of poly(ethylene-oxide) headgroups was unequivocally demonstrated, as they were seen to induce an ordering of the surface water molecules present in their direct proximity. In contrast, sugar-based moieties and other small non-ionic species, such as acetic acid and formic acid, were shown to have a rather opposite effect. The experiments shown here also suggest that the free OH resonant feature, characteristic of the pure water surface, is the result of the structuring and cooperative interactions of a certain number of water molecules in the surrounding liquid, and when these domains are perturbed the ordered water molecules with a dangling OH bond disappear from the surface. Moreover, a peculiar band common to all the non-ionic surfactant studied and assigned to water species located in proximity to the surfactant hydrocarbon tail phase in a non donor configuration, was also a remarkable result, the implications of which are yet to be unravelled.

Other important findings resulted from direct examination of the different adsorbates, targeting their specific vibrational frequencies. Noteworthy, were the formation of antiparallel double layer structures at the neat acetic acid surface, and the presence of patches of unperturbed water and hydrocarbon chains lying close to the surface plane at low surface densities of C_{12}E_{5} solutions. Additionally, the orientation of the surfactant molecules at different surface densities like the sulphate headgroup of SDS or the fluorocarbon chain and carboxylate headgroup of the fluorocarbon surfactant APFN, were also characterized. The knowledge of the orientation of the surfactant molecules at the air-liquid interface is a fundamental step in understanding the correlation between molecular attributes and macroscopic properties such as foam or emulsion stability.
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