

# Forschungspraktikum: AK Prof. Motschmann

BREAKING THE SYMMETRY OF IONS AT THE AIR-WATER INTERFACE

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In this contribution we investigate the impact of the fluid-air interface on the dissolved electrolyte Potassium hexacyanoferrate  $K_4[Fe(CN)_6]$  by infrared-visible sum-frequency generation spectroscopy (SFG) and surface tension measurements. SFG is a surface specific nonlinear optical technique that records the vibrational spectrum of the adsorbed species with little to no contribution from the bulk phase. According to the selection rules, only modes which are simultaneously Raman and Infrared active can contribute to the SFG spectrum. Since the unperturbed  $[Fe(CN)_6]^{4-}$  belongs to the point group  $O_h$ , no vibrational mode is SFG active, unless a deformation takes place. Our spectra provide experimental evidence for a symmetry reduction of the ions at the interface to subgroups with no center of inversion. The distortion of the ions is the direct consequence of the interfacial force field and is further discussed in this paper. The SFG spectra of the interfacial water were used to gain further insights in the distribution of the ions at the interface. Furthermore the combined data of the surface tension equilibrium isotherm and the SFG spectra suggest a non-monotonous interfacial concentration profile of the ion.

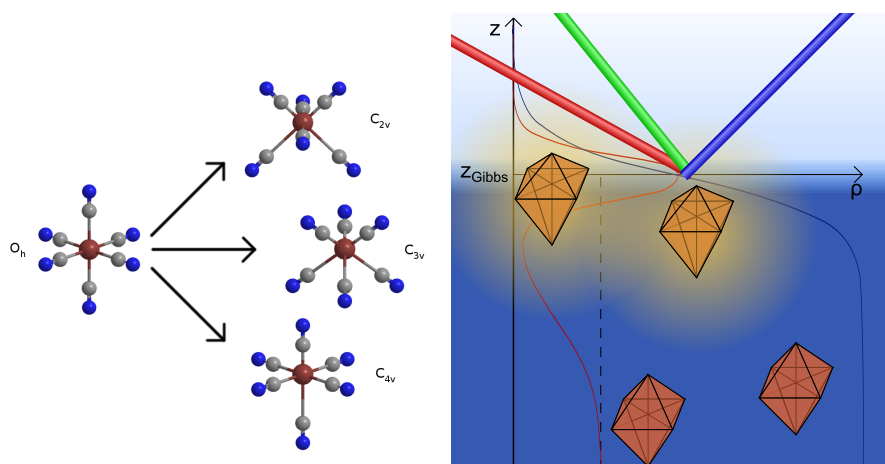


Figure 1: Possible distortions of the octahedral symmetry to conformations which are SFG active.

**Tasks:** We extend the same idea to different complexes and try to quantify the data.

**Technique:** Sum frequency generation spectroscopy

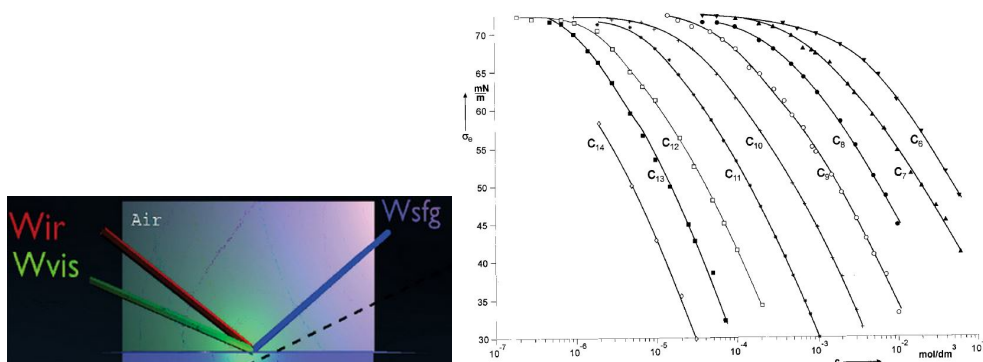
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## ODD-EVEN EFFECTS IN A HOMOLOGEOUS SERIES OF SURFACTANTS INVESTIGATED BY SFG

### 1 Sum frequency generation SFG

Sum frequency generation spectroscopy is an interface specific nonlinear optical spectroscopic technique. The spatial and temporal overlap of a tunable IR ps-pulse and a visible pulse at the interface generates a signal at the sum frequency. Scanning the infrared frequency yields a vibrational spectra to which only the adsorbed molecules contribute.



### 2 Odd-even effects of dimethyl-phosphine-oxides

The homologous series of alkyl-dimethyl-phosphine-oxides is a well characterized<sup>[1]</sup> group of surfactants. Depending of the chain length of the alkyl chain, a variation for the characteristic area per molecule as obtained from fitting by the Frumkin-adsorption isotherm model is observed. Even though the area per molecule is larger than the diameter of the headgroup the  $\pi(A)$ -isotherm<sup>[2]</sup> alters markedly depending on odd or even alkyl chain length. It is the aim of this study to clarify the influence of conformational order on this effect by investigating the SFG-spectra of respective aqueous solutions of several members of the homologous series at various concentrations.

### References

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- [2] K. Lunkenheimer, K. Haage, and R. Hirte, "Novel results on the adsorption properties of n-alkyldimethylphosphine oxides at the air/water interface.," *Langmuir*, vol. 15, no. 4, pp. 1052–1058, 1999.

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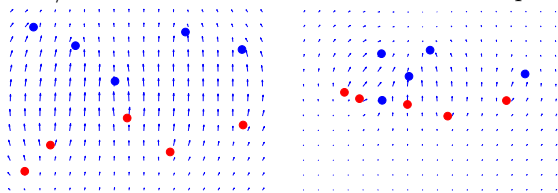
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### WHY DO IONS ACT IN A SPECIFIC WAY?

The distribution of ions at a charged interface defines one of the central themes of Colloids and Interface Science. On a mean field level, the ion profile is described by the Poisson-Boltzmann theory which captures electrostatics and thermal motion. However, this treatment has a severe shortcoming. It predicts that ions of the same diameter and valence behave in a similar fashion which is not the case.

There are many manifestation of ion specific effects in soft matter system. The solubility of small molecules such as benzene in aqueous solution depends strongly on the nature of the added salts. All salting in and salting out effects are strongly influenced by the presence and the nature of the dissolved electrolytes. The solubility of proteins in aqueous solutions is governed by electrolytes in an ion specific fashion. The catalytic activity of certain enzymes depends strongly on the nature of the salts. The roughness and the thickness of polyelectrolyte multilayers depend on the nature of the ions. The analysis of all these phenomena leads to the Hofmeister sequence of ions and its existence and widespread applicability suggests an underlying common principle. The key question is why do ions act in a specific way? Are we able to identify simple concepts that predict the behaviour of a salt solution in a certain experiment?

The goal of this paper is a comparison of aqueous electrolyte solution in the bulk and at the liquid-air interface using different combinations of hard ( $\text{Cl}^-$ ,  $\text{Li}^+$ ) and soft ions ( $\text{I}^-$ ,  $\text{Cs}^+$ ). In particular, we were interested in the conditions under which ion pairs form at the surface and whether this is linked to ion-pairing in the bulk. Ion hydration and possible ion association in the bulk was probed with dielectric relaxation spectroscopy (DRS). This technique monitors the cooperative reorientation of the dipolar solvent molecules and detects all ion-pair species possibly present in the solution. At the interface, the formation of contact ion pairs was investigated by Infrared-Visible-sum frequency spectroscopy (SFG). This nonlinear optical technique possesses an inherent surface specificity and can be used for the characterization of interfacial water. The intensity of the SFG active vibrational stretching modes depends on the number of oriented water molecules. The electric field at the surface of a charged aqueous interface aligns the water dipoles, which in turn increases the SFG response. Hence, the enhancement of the oscillator strengths of the water vibrational modes can be used to draw some conclusions on the strengths and geometrical extension of the electric field. The formation of ion pairs at the interface reduces the intensity of the hydrogen bonded water band. The underlying theory is presented. The combined data show that there are no contact ion pairs in the bulk of the fluid and —at best— only small amounts of solvent shared ion pairs. On the other hand, the combination of hard/hard or soft/soft ions leads to the formation of ion pairs at the liquid-air interface.



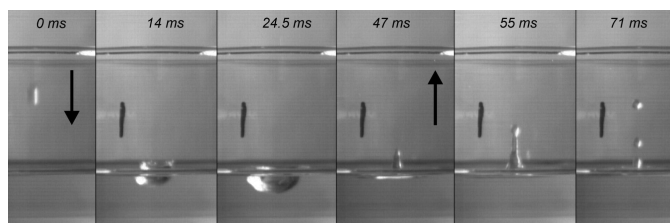
Eva Brandes, Christiane Stage, Hubert Motschmann, Julian Rieder and Richard Buchner Is surface layering of aqueous alkali halides determined by ion pairing in the bulk solution? J. Chem. Phys. 141, 18C509 (2014); <http://dx.doi.org/10.1063/1.4895969>

**Technique:** Sum frequency generation spectroscopy and dielectric relaxation spectroscopy

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### THE IMPACT OF THE IMAGINARY PART OF THE SURFACE DILATATIONAL MODULUS ON THE SPLASHING BEHAVIOR OF DROPS



The relation between the complex surface dilatational modulus  $E$  of aqueous surfactant solutions and the splashing behavior of their drops on liquid surfaces is investigated. The surface dilatational modulus  $E$  of selected surfactant systems has been determined in the frequency range of 3-500 Hz by means of the oscillating bubble technique. According to the functional dependence of the phase of the complex module  $E(\omega, c) \exp i\phi(\omega, c)$  at higher frequencies adsorption layers can be classified as surface elastic or surface viscoelastic. Each shows pronounced differences in drop splashing experiments. The impact of a drop onto the liquid was monitored with a high speed camera. The data establish a clear relation between imaginary part of the surface dilatational modulus  $E$  and the height of the drop rebound. These findings may be of importance for formulations in crop protection.

We all expect to have fresh and high quality food at our disposal serving our nutritional needs at an affordable price. Chemical crop protection is a crucial element in controlling the diseases threatening our food supply<sup>[?]</sup>. Nevertheless pesticides jeopardize the environment and there is a trade-off between benefits and environmental cost. On the one hand soil can be degraded of organisms living in it but on the other hand the misuse or overuse of pesticides can lead to severe damage. Great care should be taken to target solely the foliage and avoid spray drifting or off-target contamination. In this paper we demonstrate that a careful adjustment of the surface rheological properties of the applied pesticides formulation may help to minimize these undesired side effects.

A plant protecting formulation gets nebulized and sprayed on a leaf. The impact of the drop should be governed to a large extent by dynamic surface properties, disregarding adhesion forces between foliage and the crop protecting agent. The first contact between a contact area and a drop involves a deformation of its surface. Hence we expect the dynamic surface properties - particularly the surface dilatational modulus  $E$  - to have a strong impact on the splashing behavior of the drop.

**Technique:** Oscillating bubble technique, high speed camera

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## EFFECT OF ELECTROLYTES ON BUBBLE COALESCENCE



The foaminess of ocean waves, relative to fresh water, has long been attributed to the effect of salts in reducing bubble coalescence. This phenomenon is exploited in extraction processes using froth flotation, in which the extraction efficiency increases as the bubble size gets smaller. But whereas the bubble-stabilizing effect of surfactants is well understood, the effect of salts is not; the fact that salts decrease the surface tension of water and that they are desorbed from the air–water interface would, if anything, be expected to destabilize bubbles. The bubble coalescence is inhibited by some salts whereas others have no effect and that this inhibition occurs only upon the 'matching' of a two-valued empirical property assigned to each anion and cation.

We have some new ideas about the mechanism and conduct some well defined experiment in a home build set-up

Christian Luigs

**Technique:** high speed camera and a home build device

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