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**Investigation of Interfaces
by Sum-Frequency Generation Vibrational Spectroscopy**

Ph.D. Thesis

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1. Introduction and aims

The investigation of interfaces and of the processes and reactions that takes place at interfaces is under continuous development owing to the new methods becoming available in this field. As all the materials are in contact with their surrounding phases through interfaces, the more precise knowing and mapping of interfaces is in the focus of scientific interest. The properties of the interface – besides, that they might be very different from that of the bulk phase – are characteristic regarding the future function and use of the material in question.

With the traditional surface analytical techniques and instrumentation – instead of the more complex interfaces – only the investigation of well-defined model systems were possible, at ultra high vacuum (UHV) and low temperature conditions. One of the major tasks of the modern surface research – besides model systems – is to gain information about surface chemical processes under realistic conditions (for example abrasion-, temperature- and corrosion-resistant coatings or other functional elements).

The optical spectroscopic techniques – for example, Sum-Frequency Generation Vibrational Spectroscopy (SFG) which is based on a second order nonlinear optical effect – due to its surface specificity and submonolayer sensitivity offer an excellent opportunity for molecular level investigation and for any kind of interfaces (e. g. liquid/solid, liquid/liquid or gas/solid, even at high pressure gas conditions).

Combining and using Sum-Frequency Generation Spectroscopy with another surface analytical methods in the field of surface science and heterogeneous catalytic research makes possible not only the investigation of well-defined model system but complex interfaces as well.

The chemical composition, morphology and the electronic structure of the interfaces can be characterized simultaneously, and in case of adsorption processes we can also get information about the feature of adsorbed molecules and intermediates. This can contribute to the synthesis of new and more effective materials (coatings, catalysts).

The Ph.D. dissertation demonstrates via three examples the great applicability of Sum-Frequency Generation Spectroscopy in the study of such surfaces that are hard to examine using other techniques.

During the experiments applying parallel the traditional surface analytical techniques (X-Ray and Ultraviolet Photoelectron Spectroscopy (XPS, UPS), Scanning

Tunneling Microscopy (STM) together with Sum Frequency Generation Spectroscopy we have studied the surfaces and the processes at the interfaces.

The aim of the dissertation was to show that the complex surface analytical setup of our laboratory is capable to provide new information also about interfaces that not at all or hardly could have been investigated before.

2. Applied instruments and experimental methods

For the experiments that are introduced in the dissertation I used surface spectroscopic methods: Sum-Frequency Generation-, X-Ray and Ultraviolet Photoelectron Spectroscopy and Scanning Tunneling Microscopy in order to investigate different interfaces.

The experimental setup consists of two parts: an ultra-high vacuum surface analysis system and a Sum-Frequency Generation Vibrational spectrometer. The UHV system is equipped with an electron beam evaporation source and a fine focus ion gun for sample preparation, a dual-anode X-ray source and a gas discharge lamp for X-ray and ultraviolet photoelectron spectroscopy. The vital part of the system is an SFG chamber, which was designed especially for this setup. In which experiments can be performed from ultrahigh vacuum to atmospheric pressures. The sample temperature can be varied between 150-900 K. Laser beams necessary for SFG measurements are introduced into the chamber via large CaF₂ windows.

The Sum-Frequency Generation Spectrometer provides two possibilities for sample measurements: the first possibility is when the sample is exposed to atmospheric conditions and the second one is when the sample is housed in the UHV-high pressure cell of the surface analytical system.

This setup provides a unique environment to study interfaces under in situ conditions by a combination of complementary techniques, and to characterize the vibration frequencies of the interfacial species, the surface composition and electronic structure simultaneously.

Sum-Frequency Generation Vibrational Spectroscopy is a second order nonlinear optical spectroscopic technique with submonolayer sensitivity. The method is surface specific in most of the cases, as second order nonlinear optical processes are forbidden in the bulk of centrosymmetric media (e.g. metals, liquids, gases, etc.),

therefore the sum-frequency signal is generated only at interfaces where the centrosymmetry is necessarily broken. The Sum-Frequency Generation Spectroscopy provides the characteristic vibration frequencies of the interfacial species, while band intensities are connected to number of the molecules at the interfaces and also provides information about the orientation distribution of these molecules.

The traditional surface analytical methods, as XPS and UPS are photoelectron spectroscopic techniques that can be used to determine the elemental composition, electronic- and chemical state of the elements in the surface of the sample and can be also used for quantitative analysis.

By the Scanning Tunneling Microscopy measurements we can get information on the electronic structure and geometry at a given location in the sample at the atomic level.

3. Experimental results, and new scientific findings

3.1. Adsorption of cationic surfactant at the air/water interface

The cationic surfactants are defined as salts of an amphiphilic anion with an amphiphilic cation. These molecules are migrating spontaneously from their own water solution onto the air/water interface, thus creating an equilibrium adsorption layer at the surface. I investigated the adsorption properties of two kinds of symmetric chain cationic surfactants: octyltrimethylammonium octyl sulfates (OTA-OS) and dodecyltrimethylammonium dodecyl sulfates (DTA-DS). Applying Sum-Frequency Generation Spectroscopy I followed the changes take place at the air/water interface as the function of the bulk surfactant concentration.

- Based on SFG measurements I identified the phases that were formed at the interface. At low bulk concentration the surfactant molecules create a gaslike phase, while at higher concentrations a condensed liquidlike phase in the equilibrium adsorption layer.

• I established that by increasing the bulk concentration of the dodecyltrimethylammonium dodecyl sulfates catanionic surfactant the monolayer turns from a gaslike phase to a liquidlike phase at a constant chemical potential, which means that a two-dimensional first-order phase transition takes place in the adsorption layer. While in case of the shorter chain length – octyltrimethylammonium octyl sulfates – catanionic surfactant there is no phase transition.

• Concerning the structure of the absorption layers based on the analysis of the Sum-Frequency Generation spectra I determined that the alkyl chains of cationic surfactant molecules have many gauche-defect and they are not in all-trans conformation.

3.2. The characterization of Langmuir-Blodgett monolayers

I studied the features of Langmuir-Blodgett (LB) monolayers of octadecanoylhydroxamic (C18N) acid and octadecylphosphonic acid (C18P) prepared on glass, iron and copper substrates with the help of XPS and SFG spectroscopy on air/solid interface. Based on our preliminary experiments these monolayers seem to have anticorrosive effect and prohibiting the adhesion of microorganisms. I could determine the structure, homogeneity and ordering of the layers and orientation distribution of the terminal methyl groups by Sum-Frequency Generation Spectroscopy. And with the help of XPS measurements I gained additional information about the thickness of the LB monolayers, the chemical states of the substrate and the interaction between the substrates and the headgroups.

I demonstrated that well-ordered monolayers were formed by the Langmuir-Blodgett technique on both metal substrates investigated, based on Sum-Frequency Vibrational spectra.

• With the fitting and evaluation of the Sum-Frequency spectra I determined the orientation distribution of the terminal methyl groups. The upper limits for the mean tilt angle (closed by the sample surface normal and the symmetry axis of the terminal methyl groups) of the terminal methyl groups in the ordered structure of the predominantly all-trans alkyl chains are $\sim 20^\circ$ for C18N and $\sim 10^\circ$ for and C18P. Knowing this structural information I concluded that the alkyl chains of the C18N, C18P molecules are nearly perpendicular to the substrate surface.

- The XPS measurements also supported that the of the LB layers was successful in spite of the fact the hydrophobic contamination layer is still present on the metal substrate during the formation of the monolayer; and the molecules are connected to the substrate via their headgroups.

- According to the results of the XPS measurements and DFT (Density Functional Theory) calculations the thickness of the layers of the hydrocarbon tails of C18N and C18 P molecules are typically 1.9-2.1 nm, while the layer of headgroups is some 0.3-0.35 nm thick and the total length of the C18P and C18N molecules is around 2.4-2.5 nm. The tilt angle of the carbon chains to the surface normal is about 20-30°. The obtained results agree well with that of coming out from SFG measurements.

- During the investigation of the bonding mechanism between the C18N, C18P molecules and the transitional metals substrates I established that the headgroups of the long-chain alkyhydroxamic acid and alkylphosphonic acid molecules are partially or completely deprotonating after the deposition of the LB layers. I pointed out that the number of the surface hydroxyl groups of the copper substrate has decreased upon LB film deposition.

- **I demonstrated that condensation-type interaction takes place during the deposition: a bond is formed between the deprotonated headgroup of octadecanoylhydroxamic acid and octadecylphosphonic acid and the surface -OH groups of the substrate, which is accompanied by the elimination of water molecules.**

3.4. The characterization of Self Assembled Monolayers (SAMs)

With the self-assembly process practically it is much easier to create monolayers on metal substrate, than by using the Langmuir-Blodgett technique. That was the reason for us to analyse how to develop spontaneous self-assembled layers from the solutions of octadecanoylhydroxamic acid and octadecylphosphonic acid on copper and iron substrate. I followed the time dependence of self-assembly process by Sum-Frequency Generation Spectroscopy.

- **With the help of time-dependent Sum-Frequency spectroscopy measurements I demonstrated that from the solution of octadecanoylhydroxamic acid and octadecylphosphonic acid molecules in the course of a spontaneous self-assembly process ordered layers are formed with homogeneity and ordering similar to LB's.**

3.5. Carbon monoxide adsorption on gold surfaces

Most part of the investigations in the field of surface science and heterogeneous catalytic research concentrates onto the design and examination of model-systems.

In the introduced series of experiments the first elementary step of carbon monoxide oxidation, namely the adsorption of carbon monoxide molecules was investigated on gold surfaces.

- I found – in accordance with the corresponding literature and the results of the theoretical calculation – that carbon monoxide does not adsorb in measurable quantity even at elevated pressures up to 1 mbar on intact Au(111) single crystal surface in the 160-270 K temperature range.

- I demonstrated that carbon monoxide interacts with the roughened Au(111) surface (300 K, 10 min, 3 keV) in wide pressure and temperature range. Presumably sputtering increased the number of Au atoms located at step edge and kink sites. These low coordination gold atoms are which take place in the carbon monoxide adsorption. This result is confirmed by adsorption energy data from theoretical calculations.

- The pressure-dependent Sum-Frequency spectra showed that the peak positions shift towards lower wave numbers as the CO pressure is increased (10^{-8} -1 mbar). These behaviours is opposite to the one was observed in case of transition metals.

- **I established that Au(111) surfaces modified by Ar ion bombardment adsorb carbon monoxide above the desorption temperature for traditional UHV surface science studies (190-200 K). Fitting of our SFG spectra indicated that all spectra could be quite well described by a single, narrow vibrational resonance, which means that the carbon monoxide molecules adsorbed at the same geometry type or at equivalent adsorption sites.**

• The XPS and STM measurements supported that at room temperature in the presence of CO gas due to the interaction between carbon monoxide molecules and sputter modified Au(111) surface a significant part of the surface gold atoms rearrange, but the carbon monoxide molecules do not adsorb permanently onto the surface. Due to his carbon monoxide induced reordering the roughened Au(111) surface relaxed, and surface- and electron structural states became characteristic to the Au(111) single crystal.

4. Publications directly related to the dissertation:

1) Varga, I.; Keszthelyi, T.; Mészáros, R.; **Hakkel, O.**; Gilányi, T.; *Observation of a liquid-gas phase transition in monolayers of alkyltrimethylammonium alkyl sulfates adsorbed at the air/water interface*
J. Phys. Chem. B 109 (2005) 872

IF₂₀₁₀: 4.189

2) Keszthelyi, T.; Pászti, Z.; Rigó, T.; **Hakkel, O.**; Telegdi, J.; Guzzi, L.; *Nemlineáris optikai módszer határfelületi jelenségek in-situ vizsgálatára: az összegfrekvenciakeltési spektroszkópia és néhány alkalmazása*
Magy. Kém. Foly. 111(2) (2005) 70

IF₂₀₁₀:0.00

3) Keszthelyi, T.; Pászti, Z.; Rigó, T.; **Hakkel, O.**; Telegdi, J.; L. Guzzi, L.; *Investigation of solid surfaces modified by Langmuir-Blodgett monolayers using Sum-Frequency Vibrational Spectroscopy and X-ray photoelectron spectroscopy*
J. Phys. Chem. B 110 (2006) 8701

IF₂₀₁₀: 4.189

4) **Hakkel, O.**; Pászti, Z.; Keszthelyi, T.; Frey, K.; Guzzi, L.; *Study of FeOx/Au inverse model catalysts by in situ Sum-Frequency Generation Vibrational Spectroscopy*
Reac. Kin. and Cat. Lett., 96 (2) (2009) 345

IF₂₀₁₀: 0.61

5) **Hakkel, O.**; Pászti, Z.; Frey, K.; Keszthelyi, T.; Berkó, A.; Guzzi, L.; *In situ sum frequency generation vibrational spectroscopy study of CO adsorption on Au surfaces promoted by Ar⁺ sputtering and FeO_x additives*
Cat. Today, submitted (2010)

IF₂₀₁₀: 3.00

6) Pászti, Z.; **Hakkel, O.**; Keszthelyi, T.; Berkó, A.; Balázs, N.; Bakó, I.; Guzzi, L.; *Interaction of carbon monoxide with Au(111) modified by ion bombardment: a surface spectroscopy study under elevated pressure*

Langmuir, sent for publication

Total impact factor: 11.98

5) Other papers:

1) Kiss, E.; Keszthelyi, T.; Kormany, G.; **Hakkel, O.**; *Adsorbed and spread layers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers at the air-water interface studied by Sum-Frequency Vibrational Spectroscopy and tensiometry*

Macromolecules 39(26) (2006) 9375

IF₂₀₁₀: 4.27

2) Pászti, Z.; Keszthelyi, T.; **Hakkel, O.**; Guzzi, L.; *Adsorption of amino acids on hydrophilic surfaces*

J. Phys. Condens. Matter 20 (2008) 224014

IF₂₀₁₀: 2.03

5. Oral and poster presentations

1) Keszthelyi, T.; Pászti, Z.; **Hakkel, O.**; Guzzi, L.; *Investigations of interfacial phenomena of biological relevance by Sum-Frequency vibrational spectroscopy*

12th International Conference on Vibrations at Surfaces, Erice, Italy, 2007

2) Pászti, Z.; Keszthelyi, T.; **Hakkel, O.**; Guzzi, L.; *Sum-Frequency Generation: An Efficient „in situ” Tool for Interface Characterization*

TÉT Meeting, June 19, Prague, Czech Republic, 2007

3) **Hakkel, O.**; Keszthelyi, T.; Pászti, Z.; Guzzi, L.; *Határfelületek vizsgálata összegfrekvencia-keltési spektroszkópiával*

MTA KK Doki Iskola, Mátrafüred, Hungary, 2007

4) Pászti, Z.; Keszthelyi, T.; **Hakkel, O.**; Guzzi, L.; *Sum-Frequency Generation: An Efficient „in situ” Tool for Interface Characterization*

National Centre for Catalysis Research Indian Institute of Technology, Madras, Chennai, 2008

5) Kiss, É.; Keszthelyi, T.; Kormány, G.; **Hakkel, O.**; *Adsorbed and spread layers of Pluronics studied by Sum-Frequency Vibrational Spectroscopy and Tensiometry*

20th Conference of the European Colloid and Interface Society and 18th European Chemistry at Interfaces Conference, Sept 17-22, Budapest, Hungary, 2006

6) Varga, I.; Mészáros, R.; Gilányi, T.; Keszthelyi, T.; **Hakkel, O.**; Guzzi, L.; *The 2D Phase Behaviour of Alkyltrimethylammonium Alkylsulfates at the Air/Solution Interface*

11th International Conference on Surface and Colloid Science, Iguassu Falls, Brazil, 2003

7) Pászti, Z.; Keszthelyi, T.; **Hakkel, O.**; Guzzi, L.; *Adsorption of amino acids on hydrophilic surfaces*
12th International Conference on Vibrations at Surfaces, Erice, Italy, 2007

8) **Hakkel, O.**; Keszthelyi, T.; Pászti, Z.; Rigó, T.; Telegdi, J.; Guzzi, L.; *Spectroscopic investigation of surface modifications*
COST Training School, COST D30 Summer School, Liverpool, England, 2005