

Project Description – Project Proposals

Ellen H.G. Backus
Department of Physical Chemistry
University of Vienna
Währinger Straße 42
1090 Vienna, Austria
and
Max Planck Institute for Polymer Research
Ackermannweg 10
55128 Mainz, Germany

Mischa Bonn
Max Planck Institute for Polymer Research
Ackermannweg 10
55128 Mainz, Germany

Project title: The molecular scale of switchable wetting

Project Description

1 State of the art and preliminary work

Wetting phenomena are omnipresent in for example dishwashing, printing, rain drops on a window or liquid transport through pores. Different applications prefer different wetting properties. Raindrops on car windshields should not wet, but roll off. On the other hand, printing requires full wetting. Interestingly, the wetting properties depend mainly on the last molecular layer present at an interfaces: glass wets very well, i.e. has a very small contact angle, while silanized glass has a much larger contact angle.

As in principle only the last layer is important for the wetting properties, one could control the wetting by modifying just the surface layer. Moreover, if one could construct a surface that under external stimuli like pH, temperature, and light could switch between a hydrophilic and hydrophobic surface, very useful surfaces are obtained. These surfaces are used, amongst others, for controlled motion of water over a surface (1), controlled transport of water through membranes (2), or on demand self-cleaning and anti-bacterial surfaces (3). In many of these applications light is used as external stimulus. Besides for wetting surfaces responding to light have find wide relevance for medicine. For example, certain anti-cancer treatments consist of nanoparticles with light responsive coatings (4). Light could be used to release the anti-tumor drug only in tumor cells (5).

As such, these light-responsive surfaces have drawn much attention the last years (6-8). Although it is well-known that these surfaces have different wettability for different states of the photoswitch, the molecular level details are still largely unknown. Here, we aim to provide unprecedented insights into wetting phenomena at a molecular level. The results are expected to open avenues not only for a better fundamental understanding, but also for designing superior active surfaces.

It has been shown over the years that photoswitchable surfaces can be made based on, for example, azobenzene and spiropyran like molecules (9, 10). Azobenzene type molecules can be switched with UV light from the trans- to the cis-state, while blue light introduces the transition from cis to trans. Upon switching from trans to cis the dipole moment changes by 3 D

(11) resulting in a small change in the contact angle of water on top of an azobenzene coating on a flat substrate (10). Of course, side groups could be attached to the azobenzene moiety of which its exposure to the water drop depends on the state of the photoswitch. Moreover, it has been demonstrated that the contact angle for these azobenzene switches depends as well on the roughness of the substrate underneath the coating. For example, a roughening consisting of square pillars has been shown to result in a contact angle change of more than an order of magnitude larger than for a flat substrate (10).

The other frequently used molecule spiropyran can be switched between an open and closed form. As can be seen in Fig. 1 the open merocyanine form has strong absorption in the visible around 550 nm originating from the conjugated system (12). The merocyanine form is a polar zwitterionic molecule. Irradiating with visible light results in ring closure. The nonpolar spiropyran form thus formed has no absorption in the visible due to the reduced conjugation. The absorption at around 350 nm is due to the $\pi \rightarrow \pi^*$ transition in the benzopyran part of the molecule (12). The exact absorption spectrum of both derivatives depends on the side groups attached to the molecule. However, in all cases, the merocyanine absorbs in the visible region. The dipole moment of the molecules changes upon ring opening from roughly 5 D to around 20 D (13). As a result, the contact angle of water on top of a spiropyran coating is different for the two configurations. An increase of the contact angle about 30 degrees has been reported upon switching to the hydrophobic closed structure (9). Similar as mentioned above for azobenzene-based coatings, surface roughness increases the contact angle difference between the two forms. A difference of roughly 100 degrees has been reported (9).

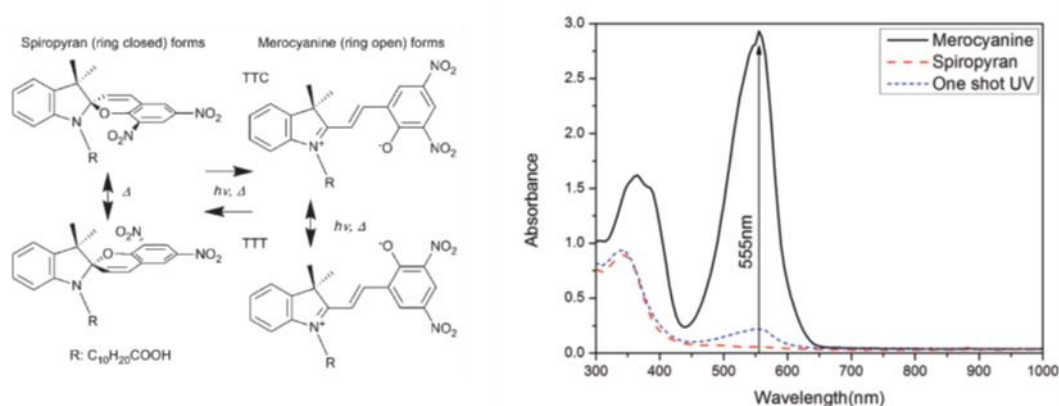


Fig. 1 (Left) Scheme illustrating the different light and temperature induced reactions for a spiropyran derivate. (Right) Absorption spectrum of the merocyanine and spiropyran form. UV light switches the unpolar closed spiropyran form into the polar zwitterionic open merocyanine form. Visible light results in the reverse reaction. The figure is taken from Ref [Photochemical & Photobiological Sciences 12, 848-853 (2013)].

It is thus well-known that this type of surfaces can be synthesized and can function as photoswitchable surfaces with changeable wettability. As such, these surfaces provide a unique way to connect molecular-level surface hydration properties with macroscopic wetting properties. In other words, these surfaces provide the possibility to optically control the molecular-level surface hydration properties. Here, we propose to follow in real-space (that is, with ~ 1 nm depth resolution near the surface) and real-time (sub-ps onwards) the molecular response to the optical modification of the surface properties, and correlate that with the macroscopic wetting angle. **In this manner, we will be able to correlate molecular-level details about water organization with macroscopic wetting properties.** We will mainly focus on spiropyran based layers as the difference in contact angle is larger than for azobenzene. Specifically, we will use molecular vibrations to obtain information about the structure, ordering, and heterogeneity of both the organic and the water part of the interface. Time-resolved vibrational spectroscopy will be used to follow the switching dynamics on the sub-ps timescale. Moreover, we will follow the spreading dynamics in the two states of the photoswitch by studying the precursor film.

In bulk systems, time-resolved vibrational and electronic spectroscopy has already been used to follow the reaction mechanism and timescale of the ring closing/opening reaction and cis/trans isomerization of the open form for spiropyran derivatives (14-17). Timescales of 1.6 and 25 ps for the ring opening and closing, respectively, have been reported for a water-soluble spiropyran (14). These experiments demonstrate the feasibility to follow the reaction dynamics of the photoswitch itself with time-resolved vibrational spectroscopy as proposed in this proposal.

For (de)wetting studies interface-specific information is required. We will not only look at the photoswitch, but we will also study the water molecules in contact with the organic layer. The method of choice to obtain molecular-level information about interfacial molecules is **sum frequency generation (SFG) spectroscopy** (18). Below, details about the experimental approaches are given. Briefly, as a second-order nonlinear technique, SFG is forbidden in centrosymmetric media (e.g., bulk water) making the technique sensitive to an interface or a surface where the symmetry is broken per definition. If one of the two incoming beams is an infrared beam in resonance with a characteristic molecular vibration, molecular sensitivity can be obtained. Here we will use infrared light in resonance with the OH stretch vibration to obtain information about the water molecules and in resonance with for example C-H, C=C, C-O vibrations to study the photoswitch. As the signal intensity is a reporter for order in the molecular groups, we could obtain qualitative information about the order in the organic layer in the two forms. Besides the type of molecular group, the vibrational frequency also provides information about the environment of the molecule. For example, the water OH stretch vibration around 3000 nm is typically very broad representing the large variety in hydrogen bonding strength between different water molecules. A stronger hydrogen bond with neighbors results in a lower vibrational frequency of the OH itself (19). Water molecules not or very weakly hydrogen bonded to neighbors have a vibrational frequency above 3650 cm^{-1} .

This static SFG method has already been used by the Backus group in collaboration with Doris Vollmer in the Butt department at the MPIP institute to link macroscopic wetting with molecular level information (20). Fig. 2a and b show the contact angle, while panel c and d show SFG spectra for two differently prepared SiO_2 windows. It is clear that the hydrophobicity depends on the number of free OH groups present at the sample; only the sample with the higher contact angle, has a clear SFG signal at 3660 cm^{-1} (right panel). Moreover, we have used static SFG to provide information about the ordering/disordering of photolipids with an azobenzene moiety in the apolar tail (21), the photo-induced crosslinking of a polymer monolayer on water (22), and the interaction of dendrimers with a model lipid membrane (23). Moreover, by looking at O-H stretch vibrations, we observed an autocatalytic dissociation mechanism for water in contact with SiO_2 (24) and bilayer-by-bilayer melting of ice (25).

In the last years, new developments have made it possible to not only measure the vibrational frequency of molecules at the interface, as done in static SFG experiments but also detect the phase of the signal. The phase provides information about the absolute orientation of the molecules, i.e., pointing in average up or down, relative to the surface plane. By combining the SFG signal from a local oscillator (typically a gold surface or a thin piece of y-cut quartz) with the SFG signal from the sample at the detector, the phase information can be retrieved in a **phase-resolved SFG** experiment (26-28). With this development, one can, for example, distinguish if the OH groups of water are pointing to, or away from, the surface and thus determine the orientation of water molecules. With this technique, it has been shown, for example, that under positively charged lipids the water molecules point with their hydrogens down, while they point up under negatively charged lipids (27). Moreover, we could show by this method that the signal at 3660 cm^{-1} at the SiO_2 water interface mentioned above originates from water pointing to the substrate and not from silanol groups (i.e. positive signal in Fig. 2e). We will use this method for the proposed work to study the orientation of water in contact with the spiropyran and merocyanine form underneath the drop but also in the precursor film.

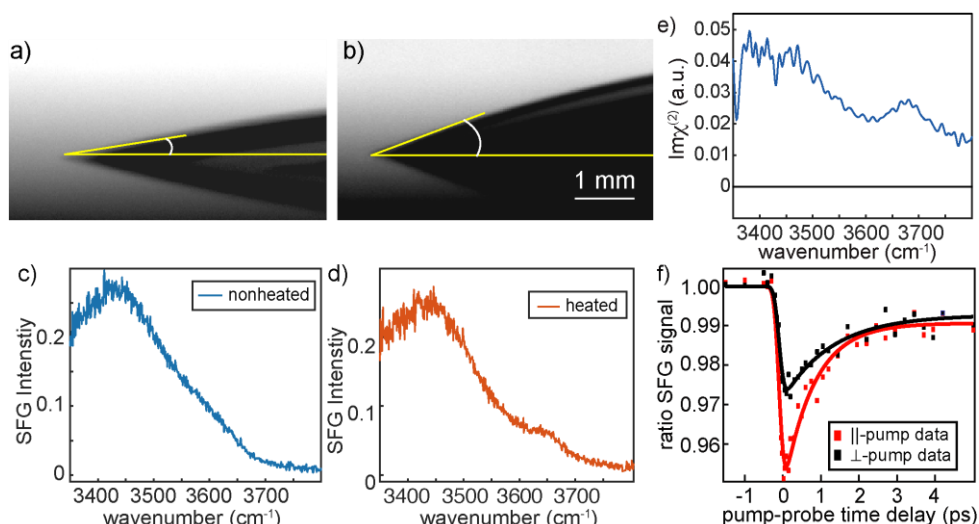


Fig. 2 Contact angle of water in contact with a nonheated (a) and heat-treated (b) silica window showing a smaller contact angle for the nonheated sample. (c, d) The corresponding SFG intensity spectra reveal a correlation between the contact angle and the 3660 cm⁻¹ quasi-free OH intensity. (e) Phase-resolved (imaginary) spectrum of the silica/water interface illustrating that the quasi-free OH peak is pointing with the hydrogen up to the silica window and thus originating from water. (f) Time-resolved SFG data of the silica/water (10 mM NaCl) interface under parallel and perpendicular polarization of pump and probe pulses. The figure is taken from Ref [Cyran et al. (2018) submitted].

Recent extensions of the method to pump/probe spectroscopy make it possible to determine heterogeneity, energy flow, and dynamics of surface reactions. Information about heterogeneity is typically obtained by pumping with varying narrow band infrared light resulting in a so-called **two-dimensional sum-frequency generation (2D-SFG)** spectrum. 2D-SFG is an expansion of two-dimensional infrared spectroscopy (2D-IR), an analog of 2D-NMR. This method was developed in the department of M. Bonn (29) and has proven by both PIs to be a powerful tool to study the heterogeneity of water molecules at an interface. For example, it was demonstrated that water underneath a negative lipid has two sub-ensembles (30), while water underneath a positive lipid consists of one relatively inhomogeneous ensemble (31). Photo-induced reactions can be followed by pumping with visible or UV light, i.e., depending on the absorption of the photoswitch, and probing with SFG. With this method, sub-picosecond time resolution could easily be achieved. Backus and Bonn developed this **pump-probe SFG** method and were the first to study the molecular motion of molecules over a surface, i.e., diffusion of CO over a stepped Pt surface. Opposite to the general accepted view that CO molecules move lateral to the surface, we could show that the CO molecule basically wiggle-waggles over the surface by making partially a rotational motion (32). More recently, we used this method to unravel the ultrafast dynamics change of the surface charge of TiO₂ and the subsequent response of water due to photo-excitation of the semiconductor (33). Pumping with infrared light provides information about the energy flow and reorientation of molecules at an interface (20, 34). A typical signal is depicted in Fig. 2f for the SiO₂ water interface. This IR pumping experiment, in turn, can give information about the binding strength of molecules at an interface.

With this toolbox at hand, our track record of using this technique to investigate wetting-relevant phenomena (20, 35), and with our longstanding experience characterizing surfaces and interfacial dynamics with the above-mentioned surface-sensitive static and dynamics methods, we are well-equipped to study the wetting behavior at the spiropyran interface. The PhD student that will be hired for the project will find him/herself in an excellent and stimulating environment to become an expert in the different sum frequency generation methods. Moreover, at the MPIP the PhD student will also be exposed to macroscopic wetting work performed in the department of Prof. Butt. In this way the applicant get trained not only in spectroscopy but also in fundamental knowledge about wetting.

1.1 Project-related publications

1.1.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

- B. Bera, O. Carrier, E.H.G. Backus, M. Bonn, N. Shahidzadeh, and D. Bonn
Counteracting interfacial energetics for wetting of hydrophobic surfaces in the presence of surfactants
Langmuir (2018) DOI: 10.1021/acs.langmuir.8b02874
- J. Schaefer, E.H.G. Backus, and M. Bonn
Evidence for auto-catalytic mineral dissolution from surface-specific vibrational spectroscopy
Nature Communications 9 (2018) 3316
- R. Khatib*, E.H.G. Backus*, M. Bonn, M.J. Perez-Haro, M.P. Gaigeot, and M. Sulpizi
Water orientation and hydrogen bond structure at the fluorite/water interface
Sci. Rep. 6 (2016) 24287 (* equally contributed)
- R.A. Livingstone, Y. Nagata, M. Bonn, and E.H.G. Backus
Two Types of Water at the Water-Surfactant Interface Revealed by Time-Resolved Vibrational Spectroscopy
J. Am. Chem. Soc. 137 (2015) 14912
- M. Bonn, Y. Nagata, and E.H.G. Backus
Molecular Structure and Dynamics of Water at the Water–Air Interface Studied with Surface-Specific Vibrational Spectroscopy
Angew. Chem. Int. Ed. 54 (2015) 5560
- D. Lis, E.H.G. Backus, J. Hunger, S.H. Parekh, and M. Bonn
Liquid flow along a solid surface reversibly alters interfacial chemistry
Science 344 (2014) 1138
- E. Haitami, E.H.G. Backus, and S. Cantin
Synthesis at the Air-Water Interface of a Two-Dimensional Semi-Interpenetrating Network Based on Poly(dimethylsiloxane) and Cellulose Acetate Butyrate
Langmuir 30 (2014) 11919
- E.H.G. Backus, J.M. Kuiper, J.B.F.N. Engberts, B. Poolman, and M. Bonn
Reversible optical control of monolayers on water through photoswitchable lipids
J. Phys. Chem. B 115 (2011) 2294
- V. Botan, E.H.G. Backus, R. Pfister, A. Moretto, M. Crisma, C. Toniolo, P.H. Nguyen, G. Stock and P. Hamm
Energy transport in peptide helices
Proc. Natl. Acad. Sci. USA 104 (2007) 12749
- E.H.G. Backus, A. Eichler, A.W. Kleyn, and M. Bonn
Real-time observation of molecular motion on a surface
Science 310 (2005) 1790

1.1.2 Other publications

n.a.

1.1.3 Patents

1.1.3.1 Pending

n.a.

1.1.3.2 Issued

n.a.

2 Objectives and work programme

2.1 Anticipated total duration of the project

Three years (01.10.2019 – 30.09.2022)

2.2 Objectives

The overall goal of the project is **to obtain molecular-level information about the (de)wetting dynamics at switchable substrates. We aim to correlate molecular-level details on the water organization with macroscopic wetting properties.** We will focus on the simple liquid water in contact with photoswitchable spiropyran based substrate. Photo-excitation triggers molecular level changes in the substrate as well as in the interfacial water structure. Therefore, these photoswitchable systems provide a unique platform for connecting the molecular-level changes to the macroscopic wetting properties. To achieve the main goal, we will pursue the following objectives, which are illustrated in Fig. 3:

Objective 1) Determining the molecular structure of the merocyanine and spiropyran monolayers in contact with liquid water and the structure, orientation, and heterogeneity of the water molecules in contact with the coating.

Sum frequency generation spectroscopy will provide a surface-specific look at the molecules at the interface. Static and phase-resolved spectroscopy will provide information about the ordering, orientation, and hydrogen bond strength in between water molecules. Interfacial heterogeneity of water molecules will be studied using 2D-SFG. We will study the system with both the open and the closed form of the spiropyran. Photodiodes will be used to prepare the desired state of the photoswitch.

Objective 2) Comparing the water structure of water under and next to drop in steady state, i.e., precursor film.

Also here, the method of choice is static and phase-resolved SFG to obtain molecular-level information about the precursor film (if that is present). If the precursor could be detected with static SFG, 2D-SFG will be used to get information about the heterogeneity of the film. This objective provides information about the difference in $\gamma_{\text{solid-liquid}}$ and $\gamma_{\text{solid-vapor}}$.

Objective 3) Determining the timescale of the photo-induced processes at the interface.

Within this objective, we study the mechanism and timescale of the photoswitching process of the spiropyran itself. We will compare the observed dynamics with available literature for bulk experiments. Moreover, we will monitor the water molecules and determine how fast the water molecules adapt to the ring closure or ring opening of the spiropyran based organic layer.

Objective 4) Determining the dynamics of the contact line spreading for the hydrophobic and hydrophilic case.

With the knowledge obtained in the other three objectives, we will, in the final step of the proposal, focus on the dynamics of the contact line spreading for the hydrophobic and hydrophilic case. We will, for example, monitor the SFG signal, using SFG microscopy, next to a

drop shortly after depositing the drop. We will also monitor the system at the edge of a drop upon switching the layer between the two states and detect the molecular level changes upon shrinking or expanding the drop.

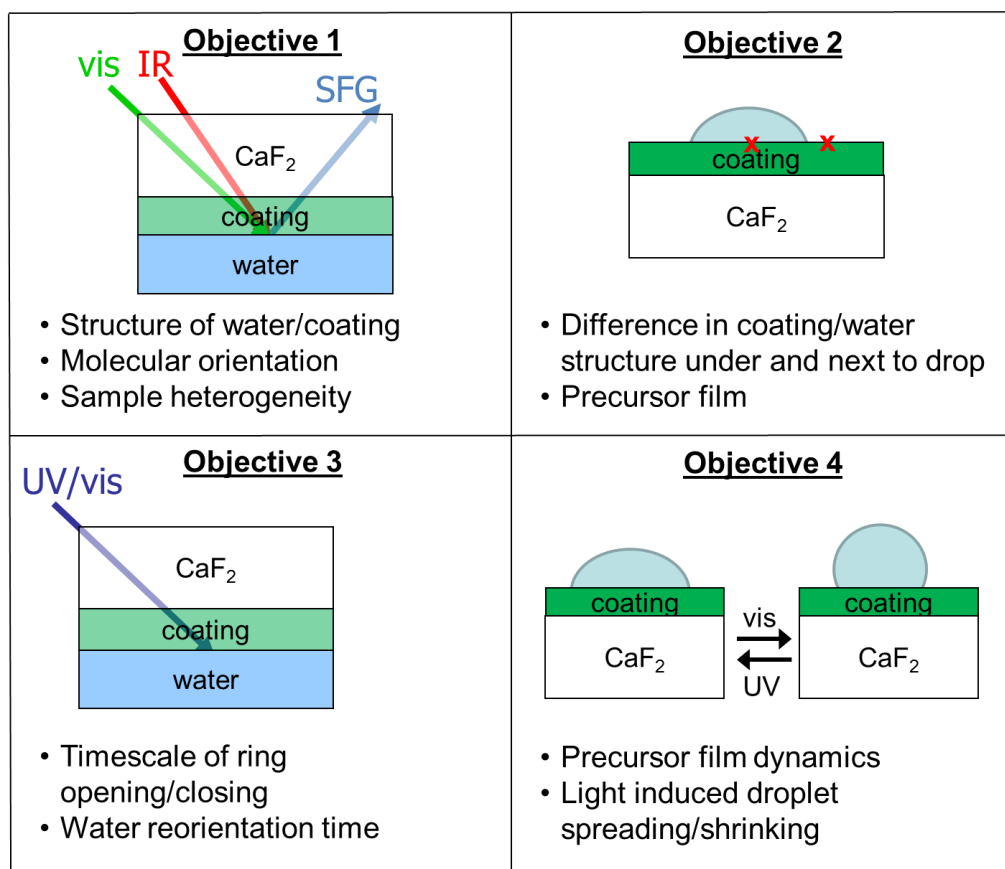


Fig. 3 Scheme illustrating the four different objectives of the proposal

2.3 Work programme incl. proposed research methods

Involved staff

Permanent/Senior staff involved

The PI Ellen Backus will supervise the project both hands-on in the lab as well as by the data analysis and interpretation and paper writing. Weekly discussions with the PI Mischa Bonn are planned to discuss data analysis and interpretation and paper writing. Regularly discussions with Daniel Bonn, a wetting expert from the University of Amsterdam, and Hans-Jürgen Butt, at the MPIP, are planned to discuss the results.

Hired staff (i.e., PhD student)

For the work described in the above objectives of the proposal, we would like to hire one PhD student. This PhD student will start the work at the Max Planck Institute in Mainz and will move with the PI Ellen Backus to Vienna, when the new labs are ready (expected for spring 2020). The equipment needed for the proposed project will be present both in Mainz and in Vienna. This PhD student will be exposed to state of the art spectroscopy methods to study the fundamentals of wetting. He/she will be trained to obtain a PhD in physical chemistry. Within the SPP the PhD student will obtain basic knowledge about the synthesis of organic layers and models/simulations to interpret the observed phenomena, besides training in wetting in general.

Samples

Within the SPP 1271, we will strongly collaborate with Prof. Haag, Freie Universität Berlin. His group will provide us with the coatings. The coatings will be deposited on 2 mm thick CaF_2 windows. As can be seen in Fig. 3, we propose to study the buried substrate. This means that the light beams have to come either from the water or from the coating side. Water has a strong absorbance in the IR making it necessary to come with at least this beam through the substrate. For experimental convenience, all light beams should come from the same direction. Thus a substrate that is transparent for IR, visible, and UV light is required. CaF_2 fulfills this criterion. We will study for the static and phase-resolved SFG flat and structured coatings and compare the spectroscopic results for the different layers. Based on the obtained results we will select a sample with the largest spectroscopic difference between the open and closed form for the time-resolved and 2D-SFG experiments. As these experiments are extremely challenging, we need a decent signal change to obtain dynamical information.

As it is known that the SFG spectrum of pure water at interfaces could be partly distorted by inter- and intermolecular coupling effects (36), we will also study isotopically diluted samples. By mixing H_2O with D_2O , these coupling effects are strongly reduced. Also in time-resolved experiments, isotopic dilution or exchange might be used to explain the observed spectral features and timescales.

Sample cells are available at the Max Planck Institute in Mainz to keep water in a closed cell. Moreover, all laser equipment is present (initially in Mainz, later in Vienna); only small experiment specific modifications might be needed. Photodiodes will be used to prepare the spiropyran system in either the closed or open form.

Below we describe in detail the experimental methods we plan to use in the project.

Research methods

Sum frequency generation spectroscopy

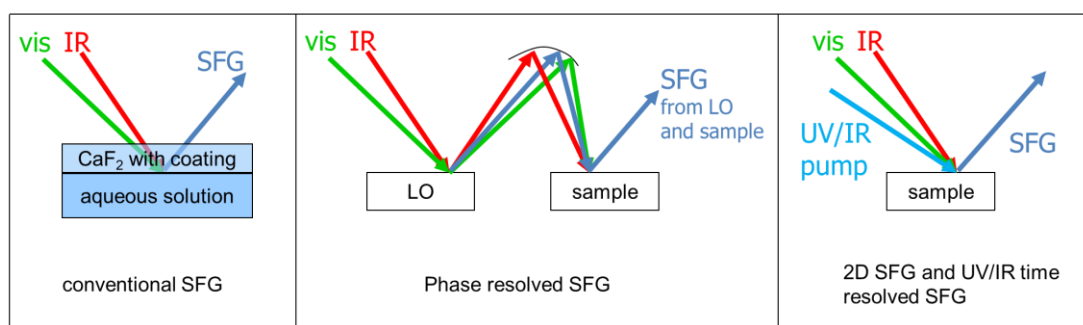


Fig. 4 Sketch of the different experimental techniques

Characterizing molecules at an interface is a challenging task, as one needs an interface specific probe that is sensitive to obtain a signal from one molecular layer and exclude the bulk signal. Sum-frequency Generation (SFG) spectroscopy (18, 37) is an optical tool that could fulfill these criteria. In SFG spectroscopy two light beams, from a pulsed laser source, providing high intensities, at frequencies ω_{IR} and ω_{VIS} generate light at their sum frequency ($\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$). The quintessential properties of the SFG process are that (i) it is allowed only when symmetry is broken; and (ii) if ω_{IR} is resonant with a molecular vibrational transition, the SFG process is resonantly enhanced. Thus, by recording the SFG signal as a function of the infrared frequency, we detect a spectrum of molecular vibrations from molecules specifically located at the interface. The first requirement makes the SFG process surface sensitive for centrosymmetric materials, as at the interface the symmetry is broken. As bulk water is centrosymmetric, SFG could measure the interfacial water molecules.

To obtain enough photons to generate the SFG signal, an amplified laser system has to be used. We use a femtosecond laser system to have enough bandwidth in the infrared laser pulse to cover a broad spectral window. We could, for example, cover the whole O-H stretch vibrational region between 3100 and 3700 cm^{-1} . By tuning the infrared source (i.e., to 3.5 or 6 μm) we could measure the spectral signatures of the spiropyran. A narrowband visible pulse is used to provide the frequency resolution for the experiment. The laser pulses originate from an amplified TiSa laser giving out 800 nm pulses of 40 fs at a 1 kHz repetition rate. Part of the laser output is frequency converted in an optical parametric amplifier in combination with a difference frequency stage (TOPAS, Light Conversion) to generate the tunable broadband IR pulses with a typical energy of 3-10 μJ . The narrowband visible pulse is obtained by passing another part of the laser output through an etalon resulting in pulses with a bandwidth of typically 15 cm^{-1} and an energy of ~ 20 μJ . Both beams are spatially and temporally overlapped at the sample (see left panel of Fig. 4). The SFG light (roughly between 630 and 730 depending on the IR frequency) will reflect from the interface and is subsequently sent into a spectrometer and detected by an electron-multiplied charged coupled device (EMCCD).

Polarisers and half-wave plates will be used to control the polarization of the incoming and outgoing beams. SFG spectra under different polarization combinations will be measured to obtain information about the orientation of especially the organic layer.

Phase-resolved sum frequency generation spectroscopy

In conventional SFG spectroscopy as described above the square of the molecular response is measured, so that the phase information is lost. The phase information is valuable since it contains information on the absolute orientation of interfacial molecules (e.g., whether the water molecules' OH groups are pointing towards or away from the interface). The development of the SFG technique into phase-specificity will allow us to obtain the phase information. By combining the signal from the sample with a local oscillator (SFG signal from a thin piece of y-cut quartz) at the detector, the phase information can be retrieved (27, 38). Recent developments, partly made by the Backus/Bonn group in Mainz, made phase-resolved experiments at buried interfaces possible (20, 39). The phase-resolved SFG process is schematically illustrated in the middle panel of Fig. 4. With this development, we can distinguish if the oxygen or hydrogen atoms of water in contact with the organic layer are pointing to the bulk water or to the organic layer. One possibility could be that water underneath the hydrophobic closed form points with a free OH (i.e., O-H group at a high frequency that is not H-bond to a neighbor) up to the substrate as has been observed for the SiO_2 interface (20). For the hydrophilic zwitterionic open form, this peak might be absent. The absolute orientation of water in the –if present- precursor film could also be obtained. Moreover, we could also determine the absolute orientation of the molecular moieties of the spiropyran derivatives.

Two-dimensional sum frequency generation spectroscopy

Two dimensional IR spectroscopy, an analogy of 2D-NMR, is a powerful technique to determine molecular structure and dynamics (40). The PI Backus has used 2D-IR previously to determine the structure of an azobenzene-based photoswitchable peptide in solution (41). The expansion of this method to surface specific 2D-SFG has been used by the Bonn department to measure the heterogeneity of water molecules at an interface (42). In 2D-SFG a narrowband infrared pump pulse is used to vibrationally excite a subset of water molecules by burning a spectral hole. At a specific time afterward the SFG probe pair measures the SFG response of the sample. By scanning the pump frequency and probing the SFG response, a 2D spectra will be obtained from which the heterogeneity can be unraveled. The unpumped response is subtracted from the pump-induced response so that solely the effect of the pump pulse can be measured. The shape of the 2D spectrum can be used to determine the heterogeneity of the system. Fig. 5a shows a 2D-SFG spectrum for a homogeneous ensemble as the SFG response is independent of the equation frequency, i.e., all water molecules are equal. On the contrary, as illustrated in Fig. 5b, if several sub ensembles are present the 2D spectrum consists of a narrow band along the diagonal; only response at the excitation frequency will be observed. In that case, the system is completely inhomogeneous, and the 2D spectrum will consist of a

narrow band along the diagonal. Moreover, a 2D spectrum could provide information if certain molecular ensembles are coupled. Coupling will result in cross-peaks as illustrated in Fig. 5c. Performing 2D-SFG experiments at different waiting times (variable time between pump and probe) results in energy transfer times and timescales of the apparent loss of heterogeneity. Fig. 5d shows a 2D-SFG spectrum of the D₂O-air interface. In the current proposal, we plan to study the heterogeneity of water molecules in contact with the spiropyran layer. We will compare the heterogeneity for the open and closed form. Moreover, by exciting vibrations of the spiropyran and probing water or vice versa, energy transfer between the organic group and water could be measured. Moreover, cross-peaks in the 2D spectrum between vibrations of the organic layer and water indicate which molecular group of the spiropyran is close to the water; the strongest cross peak is expected for the closed neighbor.

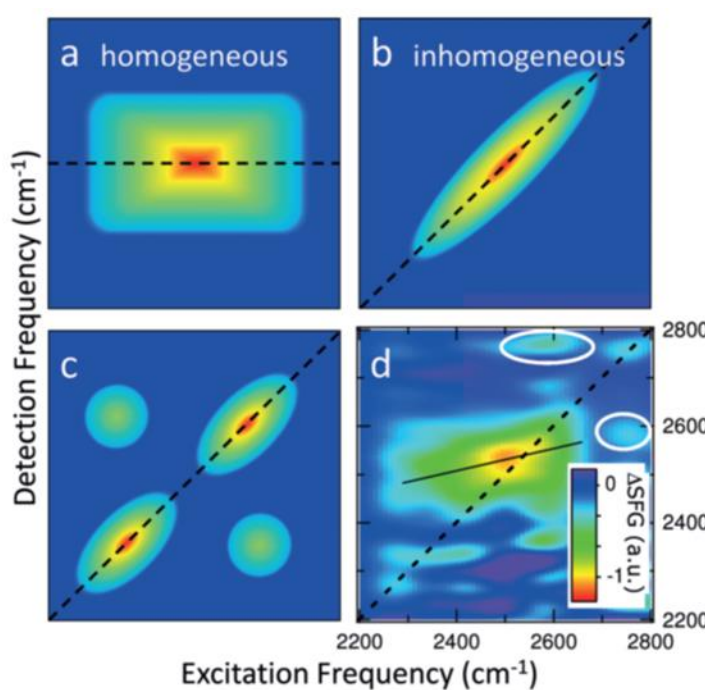


Fig. 5 Two dimensional sum frequency generation spectra for (a) homogeneous ensemble, (b) inhomogeneous ensemble, (c) ensemble of two coupled species, and (d) D₂O-air interface showing coupling between the free O-D peak at 2750 and the high frequency side of the hydrogen bonding water molecules. Figure taken from *Angew. Chem. Int. Ed.* 2015, 54, 5560 – 5576.

Time-resolved sum frequency generation spectroscopy

In case one is only interested in the energy flow in the system from a specific vibrational group, the IR pump frequency does not vary. In that case, the 2D experiment is turned into an IR pump SFG time-resolved experiment. The use of femtosecond laser pulses will result in a subpicosecond time-resolution.

To unravel the switching dynamics of the spiropyran and the subsequent reorientation of the water molecules, UV and visible light will be used to initiate the photo-reaction. In this case, a UV/vis pump-SFG probe experiment is performed. To obtain dynamical information, several spectra at different delay times between pump and probe pulses are collected. This approach has been used by the applicants to unravel the motion of CO molecules over a Pt surface (32) and to observe the reorientation dynamics of water upon photo-exciting TiO₂ in contact with water (33). Here, we propose to detect both the vibrations of the spiropyran as the water vibrations to follow their reaction dynamics upon photoswitching between the two states.

Fluorescence experiment with DASPI

To confirm the presence or absence of a precursor film, we plan to use the fluorescent dye DASPI (trans-4-[4-(dimethylamino)-styryl]-1-methylpyridiniumiodide). This dye only strongly fluoresces when confined in a (sub)nanometric film (43). With this dye we have recently in a collaborative project with the group of Daniel Bonn in Amsterdam demonstrated the presence of a precursor film on a hydrophobic substrate (35).

Workplan

Below we describe for every objective the methodological approach.

Objective 1) Determining the structure of the polymer coating in contact with liquid water and the structure, orientation, and heterogeneity of the water molecules in contact with the coating.

After preparation of the layer on the CaF₂ substrate, static SFG experiments are performed at first on solely the polymer coating without water. This experiment will be used to look at the vibrations of the spiropyran moiety in the open and closed form. Photodiodes with the appropriate wavelength will be incorporated in the SFG setup to switch the layers. Appropriate filters will be used to block the light of the photodiodes in front of the detector. In a second step water will be brought in contact with the film, and subsequently, the spectrum will be measured. Besides static SFG, phase-resolved and 2D-SFG experiments will be performed on this system. To simplify the spectrum, isotopic dilution might be used. In case of problems with 2-photon fluorescence of the photoswitch (12), the visible intensity might be reduced. As the SFG signal goes with the intensity of the incoming light and the fluorescence with the square of the intensity, the relative signal strength in favor of the SFG signal will be enhanced.

Objective 2) Comparing the water structure of water under and next to drop in steady state, i.e., precursor film.

The first task of this objective is determining the presence or absence of a precursor film. This will be done by the fluorescent dye DASPI. If a precursor film is observed, SFG experiments will be performed. The experimental approach for this objective is similar to the one described in objective 1 with the difference that now a drop will be placed on the coating, while in objective 1 the full coating is in contact with a water film. Alternatively, we might consider performing experiments in a flow cell and flow a small slab of water over the surface. We could monitor the SFG signal before, while, and after the slab passes through the laser focus.

Objective 3) Determining the timescale of the photo-induced processes at the interface.

For this objective UV/vis pump and SFG probe spectroscopy will be used. We will monitor both the dynamics of the organic layer as well as the water molecules. Based on bulk experiments performed on a water-soluble spiropyran (14) we might be at the edge of the feasibility of the experiment. In case of too small signals, we will deposit the organic layer on a prism and perform the experiment in a total internal reflection geometry. Although alignment and timing issues are more challenging, the signal will be boosted by around a factor of 100.

Objective 4) Determining the dynamics of the contact line spreading for the hydrophobic and hydrophilic case.

In this objective, we will use static SFG and follow in time the signal next to a drop directly after depositing the drop on the surface. We will use a high precision xy stage to bring the drop close to the focus of the IR and VIS laser beam and use SFG microscopy to monitor the SFG signal. Moreover, we plan to follow the precursor film upon switching the photoswitch between the two states resulting in contracting or expansion of the drop. We will try to figure out what happens on the molecular level next to and at the edge of the drop.

Schematic workplan

Task	Year 1	Year 2	Year 3
Objective 1: Determining the structure, orientation and heterogeneity of water bound to the surfactant layer for the hydrophobic and hydrophilic case			
SFG for dry films	■		
SFG for water in contact with film	■		
SFG for isotopic diluted water samples in contact with film	■		
Phase-resolved SFG	■		
2D-SFG		■	
Analyzing data and write article	■	■	
Objective 2: Comparing water structure of water under and next to drop, i.e. precursor film			
SFG next to drop	■		
2D-SFG next to drop		■	
Analyzing data and write article	■	■	■
Objective 3: Determining the timescale of the photo-induced processes at the interface			
Time-resolved SFG upon photoswitching the layer with a UV pulse; determining dynamics of photoswitch and water reorientation		■	■
Modeling the data and writing publication			■
Objective 4: Determining the dynamics of the contact line spreading for the hydrophobic and hydrophilic case			
Determining the presence or absence of precursor film with the DASPI dye		■	
Measure SFG of precursor film of a spreading film		■	
Determine dynamics of contact line spreading			■
Analyzing data and write article			■

2.4 Data handling

The data and separated backups will be stored in Mainz and Vienna. The experiments will be documented in lab-journals. We will follow the DFG guidelines.

The results of the proposed work will be **published in international peer-reviewed journals**. We expect high ranked publications considering the state-of-the-art techniques at hand to achieve the proposed objectives. Typical journals of the chemical-physics community where we are used to publish are JACS, Phys Rev Letters, J Phys Chem, PCCP, Langmuir. Considering the developments undertaken here, and the possibility that we will obtain molecular-level insights into microscopic wetting, we may expect publications in higher impact factor journals such as Nature Chemistry and Nature Physics.

Besides the publications we will present the results in **oral and poster presentations** in national (German Physical Society and Bunsentagung) and international (International Association of Colloid and Interface Scientists, American Chemical Society, Time-Resolved Vibrational Spectroscopy) conferences. Every year one or two conference visits are planned to disseminate the results.

2.5 Other information

Embedding in the priority program

This proposal aims to understand the fundamentals of the (de)wetting at switchable substrates. In that sense, the proposed work fits excellently in the priority program. We will use simple liquid water and try to connect macroscopic wetting with molecular level changes initiated by photo-switching, by looking with a molecular probe at solely the interfacial molecules. This molecular approach is in our opinion a necessary addition to experiments using microscopy to look at spreading. With high-resolution microscopy, no molecular information is obtained. **To obtain a full understanding of the fundamental physics behind the (de)wetting dynamics this molecular level information is definitely needed.**

We will expand our existing collaboration with Prof. Doris Vollmer and Hans-Jürgen Butt on combining contact angle measurements with SFG experiments to connect macroscopic and microscopic wetting.

We plan to strongly collaborate with the group of Prof. Rainer Haag in Berlin. This group will prepare the coatings for us. Within the network also strong interaction with Prof. Holger Stark from Berlin is expected. He proposes to work on photoswitchable substrates from the theoretical point of view. From collaborations with other theoreticians over the years, we know that collaboration between experimentalist and theoreticians is beneficial for both. On the one hand, our experiments can provide complementary evidence for features observed in simulations. On the other hand, theory is very helpful to link the experimental observations to insight on the molecular level.

The priority program can benefit from our experimental methods as well. We could provide measurements for other groups within the program who need molecular level information about their interface. Performing a small side project will also expose the PhD student to different research questions. Along these lines we plan a collaboration with Prof. Doris Vollmer on applying SFG to characterize the properties of brushes in presence and absence of a drop and with Prof. Hans-Jürgen Butt and Dr. Rüdiger Berger we will use SFG to study solvent induced restructuring and swelling effects in front of liquid drops.

Embedding in the general SPP structure: within the travel budget money is requested for travelling to the workshop, schools, and conferences within the SPP. If it fits into the scope of the advanced school organized in the first year, one of the PI could provide a lecture about surface specific spectroscopy. Both PIs have plenty of experience with lecturing the basics of nonlinear optics at summer/winterschools. Along these lines: the PI in collaboration with the PhD student could also provide hands-on tutorials on SFG experiments.

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern

n.a.

2.7 Information on scientific and financial involvement of international cooperation partners

Prof. Daniel Bonn from the University of Amsterdam will be involved in scientific discussions. We ask only for travel money for him to come to us and for us visiting him in Amsterdam.

2.8 Information on scientific cooperation within SPP 2171

Prof. Rainer Haag, Berlin: his group will prepare the photoswitchable substrates

Prof. Holger Stark, Berlin: we will provide his group with experimental data that can subsequently be compared to simulation results. By combining experiments and theory, we aim for obtaining molecular level information.

Department of Prof. Hans-Jürgen Butt in collaboration with Prof. Doris Vollmer and Dr. Rüdiger, Mainz: we will perform macroscopic contact angle experiments in collaboration with them and conduct SFG experiments on characterizing properties of brushes in presence and absence of a drop and on solvent induced restructuring and swelling effects in front of liquid drops.

Besides the agreement to cooperate as mentioned above, the network might benefit from the surface sensitive tool we have available. As for wetting the surface structure and interaction are very important, understanding the molecular level details might be very helpful.

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4 Requested modules/funds

The total budget amounts to

Cost center	Cost
PhD student	145125 €
Consumables	35000 €
Travel	28140 €
Visiting researcher	1500 €
Publication expenses	2250 €
Total	212015 €

4.1 Basic Module

4.1.1 Funding for Staff

We would like to hire one PhD student to work on the project. The cost for a PhD student for 3 years with a 75 % appointment is 145125 € a year.

4.1.2 Direct Project Costs

As detailed below the total requested direct project costs are 66890 €.

4.1.2.1 Equipment up to Euro 10,000, Software and Consumables

For irradiation the layers to switch between hydrophobic and hydrophilic condition and for a precision xy-stage to allow SFG experiments next to a droplet we budget 5 k€. The running costs of the experiment amount 10 k€ per year reserved for D₂O, CaF₂ and SiO₂ windows to deposit the layers on, replacement of optics and diodes of the laser. The total cost for consumables is thus 35 k€.

4.1.2.2 Travel Expenses

For the PhD students we ask for money to travel each year to one national conference and to international conferences in year 2 and 3. This amounts to 500+2*3000=6.5 k€. The PI Backus asks for travel money to one international and one national conference each year, resulting in 3*3000=9 k€. At these conferences the PhD student and the PI will present the output of the project and gets input from colleagues. Moreover, we plan one two-day trip a year for the 2 PIs and the PhD student to visit Daniel Bonn in Amsterdam (3x3x400=3.6 k€) and to meetings with direct co-workers, especially for the PhD student, within the SPP (3 k€). Travelling of the 2 PIs

and the PhD student to the 4-day SPP workshop in year 1 and 2 will result in travel costs of $2 \times 3 \times 520 = 3.12$ k€, while travelling of the PhD student to the 5-day advanced school (0.6 k€) and 4-day PhD-candidate workshop (0.52 k€) will amount in 1.12 k€. Participation of all three project members at the 5-day international conference in the third year will cost $3 \times 0.6 = 1.8$ k€. The total travel costs are thus 28.14 k€.

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

Every year Daniel Bonn will visit to either Mainz or Vienna for two days. Costs are estimated to be $3 \times 500 = 1.5$ k€.

4.1.2.4 Expenses for Laboratory Animals

n.a.

4.1.2.5 Other Costs

n.a.

4.1.2.6 Project-related publication expenses

To cover part of the costs of publishing our results in peer-reviewed journals we ask for $3 \times 750 = 2.25$ k€.

4.1.3 Instrumentation

4.1.3.1 Equipment exceeding Euro 10,000

n.a.

4.1.3.2 Major Instrumentation exceeding Euro 50,000

n.a.

4.2 Module Temporary Position for Principle Investigator

n.a.

4.3 Module Replacement Funding

n.a.

4.4 Module Temporary Clinician Substitute

n.a.

4.5 Module Mercator Fellows

n.a.

4.6 Module Workshop Funding

n.a.

4.7 Module Public Relations Funding

n.a.

5 Project requirements

5.1 Employment status information

Ellen H.G. Backus, Professor in Physical Chemistry, University of Vienna, permanent, and Minerva Groupleader at the Max Planck Institute for Polymer Research in Mainz till at least October 2019.

Mischa Bonn, Director at the Max Planck Institute for Polymer Research in Mainz, permanent

5.2 First-time proposal data

n.a.

5.3 Composition of the project group

Prof. Ellen H.G. Backus, professor in Physical Chemistry, University of Vienna, and Minerva groupleader at the Max Planck Institute for Polymer Research in Mainz

Prof. Mischa Bonn, director at the Max Planck Institute for Polymer Research in Mainz

Prof. Daniel Bonn, professor in physics, University of Amsterdam

5.4 Cooperation with other researchers

5.4.1 Researchers with whom you have agreed to cooperate on this project

Prof. Rainer Haag, Berlin

Prof. Holger Stark, Berlin

Prof. Doris Vollmer, Mainz

Prof. Hans-Jürgen Butt and Dr. Rüdiger Berger, Mainz

5.4.2 Researchers with whom you have collaborated scientifically within the past three years

Collaborators of PIs outside MPIP of past 3 years

Marialore Sulpizi, Johannes Gutenberg University Mainz

Mathias Kläui, Johannes Gutenberg University Mainz

Angelika Kühnle, Bielefeld University

Marie-Pierre Gaigeot, Université d'Évry val d'Essonne

Sophie Cantin, Université de Cergy-Pontoise

Huib Bakker, AMOLF Amsterdam

Daniel Bonn, University of Amsterdam

Sander Woutersen, University of Amsterdam

Eiichi Nakamura, The University of Tokyo

Ahmed Abdelmonem, Karlsruhe Institute of Technology

Alexei Kiselev, Karlsruhe Institute of Technology

Mary Jane Shultz, Tufts University

Ian Baker, Dartmouth College

Euan Hendry, University of Exeter

Klaas-Jan Tielrooij, ICFO Barcelona

Frank Koppens, ICFO Barcelona

Xinliang Feng, TU Dresden

5.5 Scientific equipment

The molecular spectroscopy department of the Max Planck Institute for Polymer Research in Mainz has several both static and time-resolved sum frequency generation setups that can be used for the planned work. The PI Ellen Backus will build a static and time-resolved sum frequency setup in her new labs at the University of Vienna. The laser equipment needed for the project is thus available. In principal the setups are shared between a few PhDs/PostDocs, which have the advantage that a new person can learn from a more experienced person all the tricks. Moreover, in case of problems people can help each other. Shared facilities result as well in good planning of the experiment on forehand. As we have many setups, a student/postdoc has never to wait long before an experiment can be performed.

5.6 Project-relevant cooperation with commercial enterprises

If applicable, please note the EU guidelines on state aid or contact your research institution in this regard.

n.a.

5.7 Project-relevant participation in commercial enterprises

Information on connections between the project and the production branch of the enterprise

n.a.

6 Additional information

n.a.