English translation of the attachment 2

Record of scientific achievements

1. Name: Piotr Fita

2. Diplomas and scientific degrees:

a) PhD in the field of physics, specialization optics,
awarded by the Council of the Faculty of Physics, University of Warsaw on 12.05.2008

Title of the PhD thesis: *Ultrafast dynamics of photoreactive molecules*

b) MSc in the field of physics, specialization optics,
obtained at the Faculty of Physics, University of Warsaw on 05.09.2003

Title of the MSc thesis: *Femtosecond dynamics of excited states of organic molecules*

3. Information on previous employment in research institutions:

2008-present: Assistant Professor at the Faculty of Physics, University of Warsaw

2008-2010: Postdoctoral Research Fellow at the Department of Science, Geneva University

4. Indication of the achievement resulting from paragraph 16. 2 of the Act of 14 March 2003 of academic degrees and academic titles and degrees and Title in Art (Journal. Laws No. 65, item 595, as amended):

a) title of the achievement:

A series of publications associated thematically: ***From physical processes to chemical reactions at liquid interfaces – studies by second harmonic generation of light***

b) (author/authors, title/titles of publications, year of publication, publisher),

H1. P. Fita, A. Punzi, E. Vauthey, *Local Viscosity of Binary Water plus Glycerol Mixtures at Liquid/Liquid Interfaces Probed by Time-Resolved Surface Second Harmonic Generation*, J. Phys.Chem. C **113**, 20705 - 20712 (2009). Applicant’s contribution: concept of the work, measurements, analysis and interpretation of results, writing the manuscript, approx. 70%

H2. M. Fedoseeva, P. Fita, A. Punzi, E. Vauthey, *Salt Effect on the Formation of Dye Aggregates at Liquid/Liquid Interfaces Studied by Time-Resolved Surface Second Harmonic Generation*, J. Phys.Chem. C **114**, 13774 - 13781 (2010). Applicant’s contribution: coordination of the work, measurements of second harmonic generation at various dye concentrations (Fig. 8), devising a model for data analysis, interpretation of results, correcting the manuscript, approx. 30%

H3. P. Fita, M. Fedoseeva, E. Vauthey, *Ultrafast Excited-State Dynamics of Eosin B: A Potential Probe of the Hydrogen-Bonding Properties of the Environment*, J. Phys.Chem. A **115**, 2465 - 2470 (2011). Applicant’s contribution: concept of the work, measurements of transient absorption of eosins B and Y, analysis and interpretation of results, writing the manuscript, approx. 70%.

H4. P. Fita, M. Fedoseeva, E. Vauthey, *Hydrogen-Bond-Assisted Excited-State Deactivation at Liquid/Water Interfaces*, Langmuir **27**, 4645 - 4652 (2011). Applicant's contribution: concept of the work, coordination of second harmonic measurements at water/dodecane interfaces, carrying out measurements of second harmonic generation and water/decanol interfaces, analysis and interpretation of results, writing the manuscript, approx. 50%.

H5. M. Fedoseeva, P. Fita, E. Vauthey, *Excited-State Dynamics of Charged Dyes at Alkane/Water Interfaces in the Presence of Salts and Ionic Surfactants*, Langmuir **29**, 14865 - 14872 (2013). Applicant's contribution: concept of studying interfaces in presence of surface active compounds (SDS and CTAB), measurements of TRSSHG of malachite green (MG) in presence of SDS (Fig. 6), correcting the manuscript, approx. 10%.

H6. P. Fita, *Toward Understanding the Mechanism of Phase Transfer Catalysis with Surface Second Harmonic Generation*, J. Phys.Chem. C **118**, 23147 - 23153 (2014). Applicant's contribution: concept of the work, construction of the experimental setup, measurements, devising a model, analysis and interpretation of results, writing the manuscript, 100%.

c) discussion of the scientific goal of aforementioned works and achieved results including discussion of potential applications.

During centuries of the development of physics and chemistry studies of matter concentrated on insides of objects, not on their surfaces. It is understandable because the amount of matter found in monoatomic (monomolecular) layers at surfaces of macroscopic objects is incomparably smaller than in their insides. On one hand, this fact suggests (rather incorrectly) that the influence of surface atoms or molecules on properties and behaviour of a macroscopic body is negligibly small. On the other hand, it makes studies of surfaces very difficult because in most experiments the influence of surface matter is completely masked by much bigger amount of matter located inside studied bodies. Nevertheless, over the past few decades the research in the field of condensed matter turned towards surfaces. Their significance to so important phenomena as surface plasmons[1], media so surprising as topological insulators[2] and technologies so desirable as solar energetics has been finally acknowledged. Moreover, rapidly developing nanotechnologies make use of objects consisting of a small number of atoms or molecules. In such objects the amount of surface matter is no longer negligible compared to bulk one, but is comparable or even dominant. The extreme example is graphene, whose whole layer must be treated as a surface.

So far, much less attention has been paid to surfaces of liquids than of solids. This fact cannot be justified, because even though phenomena taking place on surfaces of liquids are not as spectacular as those occurring on surfaces of metals and semiconductors, properties of widespread water surfaces may determine many reactions crucial for the human existence. At the macroscopic scale this applies to the vast surface of ocean water and to water in the atmosphere, present in the form of aerosols, in particular clouds. The surface of the oceans and water droplets alike adsorb chemical molecules which are produced in both industrial and biological processes. These molecules may undergo chemical or photochemical reactions induced by solar light[3,4]. On the other hand, transport of molecules between water and the atmosphere, controlled by properties of the surface, decides on undersea reactions or even on the possibility of life existence in the depths.

On a microscopic scale, equally important are processes occurring on cell membranes which separate insides of cells from the surrounding aqueous environment. These processes include chemical reactions involving molecules adsorbed on membranes (for example medicines) and transport of molecules into and out of cells[5].

Thus, while the negligence in studies of liquid surfaces cannot be justified by their little importance, the reason for this situation can be found in difficulties of such studies. For studies of surfaces of liquids, in particular of interfaces separating two liquids, one cannot apply well established and very advanced techniques of solid state physics because usually they are based on electron, neutrons or X-rays scattering.[6] On the other hand, classical optical methods based on absorption, emission and scattering of light, applied successfully in studies of bulk liquids and solutions, fail when used for studying their surfaces because the interaction of light with the surface is completely masked by the interaction with the molecules located in deeper layers of a liquid. Only to a little extent the interaction range can be limited using the phenomenon of the total internal reflection or near field microscopy because the penetration depth of the evanescent wave is of the order of 100 nm, whereas effects related to surfaces occur in several molecular layers only (typically a few nm). Therefore, a significant progress in the field of surface research has been made only when it became possible to observe nonlinear optical processes on surfaces. In order to achieve this, a proper level of sophistication of both light sources and detection techniques had to be reached and only over the past 2-3 decades the non-linear optical spectroscopy has been recognized as a fundamental tool to study properties of surfaces and processes occurring on liquid surfaces and interfaces[7–9].

Nonlinear optics was born only after the invention of the laser which – as prof. A. H. Piekara wrote in the 60s – revealed a new face of optics. Classical light sources, the only ones available before, generated light of so small intensity that a linear approximation was always satisfied. In this approximation electric polarization of a medium illuminated with light is directly proportional to the intensity of the electric field of the incident wave. Therefore, in everyday life we can never see any nonlinear phenomena. Only laser light might have so large intensity that the linear approximation does not correctly describe electric polarization. Then phenomena related to higher-order terms in the dependence of polarization on the electric field might appear. Taking into account the quadratic term means that oscillations of polarization induced by an electric field oscillating with the frequency ω contain also a component oscillating with twice that frequency, 2ω. This, in turn, means that the medium emits an electromagnetic wave with a frequency of twice the frequency of the incident wave. This phenomenon, second harmonic generation, is the simplest non-linear effect in optics[10].

Due to symmetry reasons, second order polarizability is equal to zero in media with an inversion centre, such as highly symmetric crystals, amorphous substances, glasses and liquids. However, at boundaries of different media the symmetry is broken and second-order (in general, even-order) nonlinear processes can occur on surfaces of such bodies, even if they are symmetry-forbidden in their insides. This fact underlies nonlinear optical techniques of studying surfaces and interfaces. Their sensitivity is limited to a region, where the inversion symmetry is broken, and thus to the region which by definition can be regarded as a surface. Certain information about properties of a liquid surface can be obtained already in a relatively simple experiment in which the surface is illuminated with a laser beam and the generated light of twice the incident frequency is detected (Fig. 1). For example, one can determine the arrangement of molecules at an alkane/water interface[11] by illuminating it with a beam of intense quasi-monochromatic laser pulses. Nevertheless, knowledge gained in such a simple experiment (called *Surface Second Harmonic Generation*, SSHG) is very limited.

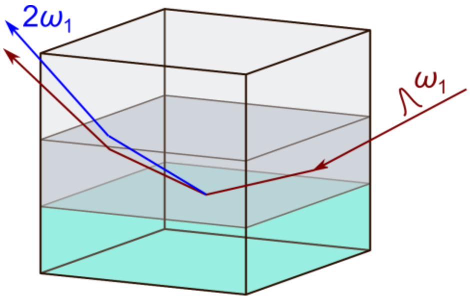


Fig. 1. Scheme of a surface second harmonic generation (SSHG) experiment.

Therefore, there are two main directions of development of nonlinear techniques for studying surfaces and interfaces. In certain experiments the surface under study is illuminated not by one but by two laser beams. At least one of them should be tuneable within a certain range of the electromagnetic spectrum. The quadratic nonlinearity in such a case leads to generation of electromagnetic waves with frequencies which are a sum (SSFG – *Surface Sum Frequency Generation*) or a difference (SDFG – *Surface Difference Frequency Generation*) of frequencies of the two incident beams. If one of these frequencies corresponds to the energy of transitions in molecules (or atoms, ions) located on the surface, the hyperpolarizability of the medium grows due to a resonance interaction of light with these molecules. The increase of the hyperpolarizability translates into an increase (even by several orders of magnitude) of the intensity of the generated wave. Therefore, by tuning one of the beams and recording the dependence of the generated light intensity on the incident beam frequency one can obtain information on the energy of electronic and vibrational levels of molecules on the surface.

The two beams illuminating the surface may belong to different parts of the electromagnetic spectrum, therefore in the most frequently used and the most powerful configuration one beam is visible and the other one is in the range of energies corresponding to molecular vibrations (mid-IR). Tuning the mid-IR beam allows recording the vibrational spectrum of surface molecules, this in turn provides information on the structure of the medium, surface concentration of selected molecules and presence and strength of selected chemical bonds (for instance hydrogen bonds). For this reason SSFG became a tool of choice for vibrational (to a lesser extent electronic) spectroscopy on surfaces[8].

The series of publications which underlie this application [**H1**-**H6**] belongs to the second direction of the development of nonlinear techniques. It involves an improvement of SSHG, so that this technique, experimentally much simpler than SSFG, could also provide valuable information on the physicochemical properties of surfaces. In principle, just by tuning the wavelength of the incident beam (further called the probe beam) and recording the second harmonic (SH) light intensity one can obtain information on the energy of electronic levels of molecules on the surface, due to the resonance enhancement, in analogy to SSFG. In case of SSHG the resonance enhancement takes place when the energy of the probe beam photons corresponds to energy of one- or two-photon transitions in molecules on the surface[9]. In most cases the two-photon resonance occurs when the doubled energy of probe beam photons is close to the difference of the energy of electronic levels. Thus, the dependence of the second harmonic intensity on the probe beam wavelength reflects the electronic absorption spectrum of molecules (Fig. 2a). In the following discussion it is assumed, for simplicity, that SSHG allows measurements of electronic absorption spectrum of molecules adsorbed on surfaces.

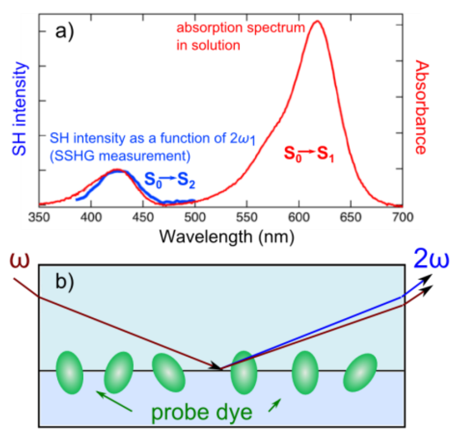


Fig. 2. a) Comparison of the absorption spectrum of a dye in solution with the dependence of the generated second harmonic intensity on its wavelength [**H5**]; b) Scheme of a second harmonic generation experiment in the presence of a probe dye on the surface.

For practical reasons, however, only transitions with the energy within the visible and near-UV range can be directly probed. This range is rather uninteresting in case of organic liquids and water. Therefore, most of the SSHG studies of liquid surfaces is carried out in systems, into which dye molecules are additionally introduced (Fig. 2b). The dye which has strong transitions in the visible range, after adsorption on the surface place a role of a probe molecule and interacts with the probe beam. Its presence results in the resonance enhancement of SSHG for appropriate frequencies of the probe beam. Obviously, the choice of the dye cannot be random because it determines (together with the way of carrying out measurements) the information obtained in the experiment. One can, for example, use a molecule whose electronic absorption spectrum depends on a selected parameter of its environment (such as polarity[12], acidity[13], ability to form hydrogen bonds[14,15] and so on) in a well-known way. Then one can record the intensity of the SH light as a function of the energy of probe photons, obtaining the spectrum of the probe dye on the surface. Analysis of this spectrum can give the value of the particular parameter in the surface layer. Alternatively, measurements carried out for various polarizations of the probe beam and of the generated SH light, can provide information on the orientational distribution of molecules on the surface[16–18]. Hence the asymmetry of forces acting on adsorbed probe dye molecules can be determined. A capability of SSHG to study physicochemical properties of surfaces is greatly enhanced when this technique is combined with chemical synthesis of dedicated probe dyes, particularly sensitive to selected properties.

An elegant example of such an approach is a study of the ability of water to make hydrogen bonds next to the boundary of water and an organic liquid using a "molecular ruler"[15]. For the purposes of these studies special probe dyes, so called molecular rulers, were synthesised. They consisted of a surfactant and a proper probe molecule, N-methyl-p-methoxyaniline (NMMA), substituted at various distances from the polar "head" of the surfactant. The electronic spectrum of NMMA depends on the ability of its environment to form hydrogen bonds as a donor or as an acceptor. Therefore, it has been determined, by recording spectra of various molecular rulers, what kind of hydrogen bonds water forms with NMMA at various distances from the interface (Fig. 3).

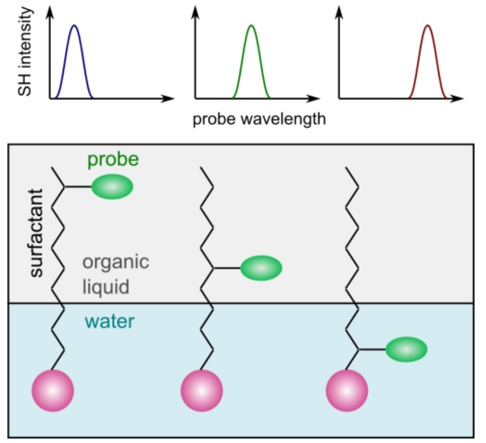


Fig. 3. Scheme of the „molecular ruler" concept for studying properties of a liquid/liquid interface[15].

The above-described scheme of studying physicochemical properties of surfaces, by using a dye – spectral probe – has a great potential but in order to fully exploit it new probe dyes have to be found and characterized. Nevertheless, it is a steady-state method which provides information on stationary values of investigated parameters, whereas from the point of view of potential studies of chemical reactions on surfaces, more useful are time-resolved techniques. SSHG can be helpful also in this case – particularly in the application to light-induced processes, underlying photochemical reactions. For such time-resolved measurements the SSHG setup must allow exciting molecules prior to their interaction with the probe beam. An additional excitation beam is used for this purpose. Both beams, pump (excitation) and probe, should be delivered by a laser generating sufficiently short pulses (pico- or femtosecond). If a pulse from the pump beam precedes a probe pulse, then the second harmonic is generated as a result of interaction between the light and molecules in the excited state. By recording the SH light intensity for various delays between the pump and probe pulses one can follow the process initiated by the optical excitation. In the simplest case the excitation changes the conditions of the resonance. For instance, if the frequency of the probe beam matches a transition from the ground state, then after the optical excitation molecules are no longer in resonance with the probe beam and the intensity of the SH light generated after the excitation drops down. As the excited molecules relax back to the ground state the intensity of the SH light returns to its initial value (Fig. 4). Numerous applications of this scheme, demonstrated for the first time in the group of Kenneth B. Eisenthal, included studies of rotations[17,19–21], isomerisation[22,23] and solvation[24–29] of molecules on surfaces of liquids as well as energy[30] and electron[31] transfer processes. Other early studies using this technique, called *Time-Resolved Surface Second Harmonic Generation* (TRSSHG), included deactivation of dimers[32] and rotations of dye molecules on a water surface[33].

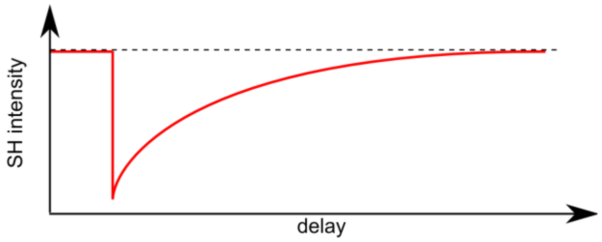


Fig. 4. Typical kinetics of the second harmonic intensity following optical excitation of molecules on the surface.

A "workhorse" of the TRSSHG method, the probe dye used to obtain resonant enhancement in many of the aforementioned works, was malachite green (MG, Fig. 5). Therefore, after joining the group of prof. Eric Vauthey at the Geneva University, where shortly before a TRSSHG setup had been built, I selected MG as the first object of my experiments in this field. An important property of MG is

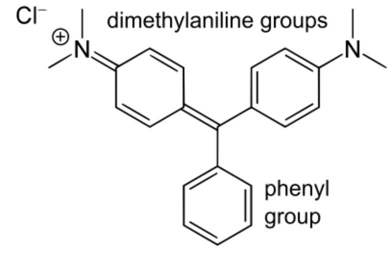


Fig. 5. Structure of malachite green (MG).

a strong dependence of the excited state deactivation rate on the viscosity of the environment. It stems from the fact that the deactivation process involves rotation of the dimetyhylaniline groups (Fig. 5). This dependence allowed using malachite green as a probe of the microscopic viscosity on surfaces[23,34]. However, earlier works had not explained all observed effects. In particular, it was not clear whether the rotation of the phenyl ring was required for the deactivation of the molecule and what was the nature of an intermediate state occurring in the deactivation pathway of the excited state.

In order to make an attempt to answer these questions we carried out detailed studies of the deactivation of MG in solutions of various viscosity (using transient absorption spectroscopy) and at interfaces separating two liquid phases whose viscosity was also varied [**H1**]. Studies in solutions of varied viscosity were carried out in binary mixtures of water and glycerol, whereas interfacial systems were constituted of such a mixture on one side and n-alkane on the other side. Viscosity at the two sides of the interfacial region was modified by changing proportions of glycerol to water and by using alkanes with a different length of the carbon chain. We carried out similar measurements also for a dye analogous to malachite green – brilliant green (BG) in which dimethylaniline groups were replaced by bigger diethylaniline groups. Our experiments showed that this modification did not change the electronic structure of the molecule but the processes involving rotations of these groups became slower due to the higher resistance exerted by the environment. Measurements of MG and BG dynamics in solutions allowed “calibration” of both dyes as probes of microscopic viscosity of their environments. The intermediate state was identified as a non-planar (with twisted moieties) form of the molecule.

During the studies of interfaces separating the water/glycerol mixture from dodecane we discovered that increasing the amount of glycerol in the aqueous phase slowed down the deactivation but this effect was less manifested at the interface than in a bulk solution (Fig. 9 in [**H1**]). At the time we proposed two possible explanations of this fact. According to the first one, the reason for the higher friction exerted on dye molecules is the more rigid water structure (resulting from a stronger network of hydrogen bonds). If this is the case, the relative effect of glycerol is smaller than in a bulk mixture at the same proportions of both liquids. The other hypothesis assumed that glycerol weakly penetrated the interfacial layer and the concentration of glycerol close to the phase boundary was smaller than in a bulk solution. These experiments inspired the group of prof. Timothy Clark to carry out molecular dynamics simulations of the systems used in our studies [**A18**]. Their results excluded the second hypothesis, by showing that the interfacial layer was actually enriched in glycerol molecules. When the bulk concentration of glycerol in the aqueous phase increased, the interfacial layer became saturated with glycerol molecules and its surface concentration increased more slowly than the bulk concentration. Hence the microscopic friction at the interface also increased more slowly than in a solution with increasing glycerol concentration.

Earlier studies of MG deactivation at water/alkane interfaces showed that the excited state lifetime did not depend on alkane’s viscosity. This result was interpreted as evidence that the rotation of the phenyl ring, located in the organic phase, is not involved in the excited state deactivation[23]. However, in those experiments the upper limit of alkane’s viscosity was only 3 cP. We have observed that if the organic phase is constituted of paraffin oil which is a very viscous ($\eta \approx 100$ cP) mixture of various alkanes, then the deactivation becomes approx. 3 times slower. This means that the rotation of the phenyl ring is actually required for the deactivation of the excited state, but this rotation determines the deactivation rate only in a very viscous environment. It is understandable because the rotation of the polar dimethylaniline groups in a polar environment (water) requires reorganization of surrounding solvent molecules, which results in a strong friction counteracting the rotation. In contrast, the rotation of the nonpolar phenyl ring in a nonpolar solvent occurs under slip boundary conditions and is much faster at comparable viscosities of the environment. Therefore, in short alkanes the rotation of the phenyl group almost freely follows the rotation of the DMA groups. Only when the phenyl ring is submerged in a very viscous liquid its rotation determines the overall deactivation rate of the excited state.

The last experiment demonstrates that TRSSHG can be also applied for studying dynamics of intramolecular processes with sub-molecular spatial resolution, by making use of localization of molecular moieties in two media which have very different physicochemical properties. This idea was later used in order to identify the mechanism of isomerization involved in the deactivation of the excited state of hemicyanines[35].

Studies of MG deactivation at water/dodecane interfaces showed that decays of TRSSHG signals depend on bulk concentration of the dye in the aqueous phase (Fig. 8 in [**H1**]). Kinetics of TRSSHG signals can be reproduced with a sum of two exponentially decaying components. The faster decay is attributed to the deactivation of the excited state of MG molecules, whereas the slower one reflects the deactivation of excited aggregates. In the discussed experiments the aggregation of the dye on a surface was an undesired effect because viscosity measurements has to be carried out at low concentrations of the dye. Nevertheless, this phenomenon became a basis for our later works [**H2**, **H5**].

In these works the effect of dye aggregation was used for measurements of concentration of inorganic ions on a water surface. Presence of ions on surfaces has long been a subject of various studies due to its importance in heterogeneous catalysis and biology. Nevertheless, classic experimental methods, such as surface tension measurements, did not provide direct information. Sometimes they even lead to incorrect conclusions, for example that the surface of aqueous solutions of salts is free of ions. Only nonlinear optical techniques, such as SSHG and SSFG can be used for direct and selective detection of ions on surfaces, by tuning probe beams to electronic[36–38] or vibrational[39–41] transitions in these ions. Studies using these methods have shown that, contrary to earlier hypotheses, there is an anions-enriched layer next to the surface of water solutions. Still, direct probing of ions involves numerous difficulties: electronic transitions in ions lie typically in the UV range, which greatly complicates detection of the SH light and SSFG measurements require sophisticated and expensive infrared pulsed laser sources. On the other hand, comparison of concentrations of different ions is difficult because they have different hyperpolarizability. Even more, measurements of the intensity of the generated SH light are prone to large errors due to problems with setting up identical geometry in different experiments. Very strong dependence of the yield of nonlinear processes on the angle of incidence of the probe beam and on refractive indices of the media surrounding the interface makes comparison of light intensities from two independent experiments questionable.

Our idea to overcome these limitations emerged from the observation that addition of an inorganic salt to the aqueous phase of the water/alkane system with malachite green usually led to an increase of the second harmonic intensity. This intensity increase was always accompanied by the increase of the amplitude of the slower component of TRSSHG signal decays. Earlier, it was noticed that addition of certain salts to aqueous solutions of MG resulted in appearance of new bands, attributed to MG aggregates, in the absorption spectrum of the dye. The excited state deactivation, observed in transient absorption experiments, was also slowed down after addition of these salts[34]. Comparison of the results of transient absorption and TRSSHG measurements led us to a conclusion that the slower component of TRSSHG decays of MG is due to deactivation of excited dye aggregates (at the time we did not have an access to an experimental setup with a tuneable probe beam but later spectral measurements with a tuneable source of femtosecond laser pulses proved this interpretation to be correct [**H5**]). The degree of aggregation of molecules on a surface is the higher, the more molecules are adsorbed to this surface. Therefore, by measuring the relative contributions of the slower and faster components of TRSSHG signal kinetics one can follow changes of the interfacial concentration of the dye. This means that relatively difficult and irreproducible measurements of second harmonic intensity, used to record changes of the interfacial concentration of adsorbed molecules, can be replaced by much more reproducible time-resolved measurements.

Systematic studies based on the idea presented above showed that addition of an inorganic salt to the aqueous phase of a water/alkane system led to an increase of MG surface concentration.

As a physical mechanism responsible for this effect we proposed electrostatic attraction between salt anions adsorbed on the surface and cations of malachite green (MG in aqueous solutions is present in a cationic form). In such a case the surface concentration of MG is related to the surface concentration of the anions. This assumption formed a basis of a simple phenomenological model of the observed phenomena, which correctly reproduced the measured dependence of the slower decay component of TRSSHG signals on the salt concentration, if aggregation occurred only on the surface and not already in the solution.

In [**H2**] we have demonstrated that TRSSHG measurements with an appropriate probe dye can be used for studying adsorption of inorganic anions. An advantage of this approach is the replacement of hardly reproducible measurements of second harmonic intensity with much more reproducible time-resolved measurements. Another advantage is a possibility of studying different anions using just one quasi-monochromatic laser which does need to be tuned in order to match absorption spectra of the anions under study. Finally, the influence of different hyperpolarizability of various anions on the results is also eliminated.

The next two works [**H3**, **H4**] are the result of a search for more probe dyes which could be used in studies of physicochemical properties of surfaces by time-resolved measurements (in [**H3**] for the first time we used the term “dynamic probe” for such a dye). Our attention turned to eosin B (EB, Fig. 6), which was used in earlier studies of surfaces[33,42], but its photophysical properties were not fully understood. In particular, the mechanism responsible for the very fast fluorescence decay in water was not explained and there were very large discrepancies in values of the excited state lifetime published in various sources[43–45]. Therefore, we started our experiments with studying the excited state dynamics of EB and comparing it to its analogue, eosin Y (EY) which does not undergo fast deactivation in solutions. The results allowed us to explain the mechanism responsible for this effect in EB.

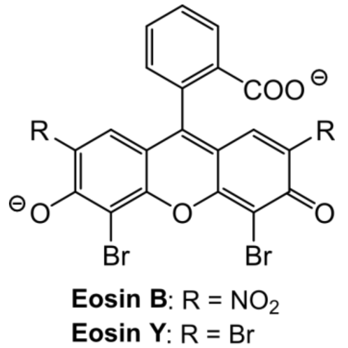


Fig. 6. Structures of eosin B and eosin Y (in doubly anionic forms).

The research tools used in these studies were steady-state absorption and emission spectroscopy and transient absorption spectroscopy with femtosecond temporal resolution. The analysis of transient absorption spectra recorded in various solvents revealed a strong correlation of the excited state deactivation rate of EB with the ability of the solvent to form hydrogen bonds as a donor. Comparison of the results with those obtained for EY together with numerical computations lead us to a hypothesis that the deactivation of the excited state of EB is caused by efficient energy transfer via hydrogen bonds formed by NO_2 groups.

These experiments showed that EB can be a dynamic probe of hydrogen bonds and its deactivation rate can be used as a measure of the ability of the environment to form such bonds as a donor. In contrast to other dyes from the same family, whose photophysical properties are also affected by the presence of hydrogen bonds, the absorption spectrum of EB remains practically the same in different solvents and only its excited state lifetime changes. This makes EB a particularly useful probe of hydrogen bonds for studies of surfaces and interfaces by TRSSHG with non-tuneable laser sources. However, its application is complicated due to strong aggregation on a water surface. In case of EB the aggregation significantly shortens the excited state lifetime and TRSSHG measurements carried out at water/dodecane interfaces in presence of EB show a strong dependence of the signal kinetics on the bulk concentration of the dye (Figs 4 and 7 in [**H4**]).

However, even at higher EB concentrations, decays of TRSSHG signals recorded at a water/dodecane interface are much slower than the excited state deactivation observed in bulk water. This means that molecules adsorbed at the interface do not undergo the process leading to the fast deactivation, so they are involved in hydrogen bonding with water only to a little extent. There might be two reasons for that: either water molecules located close to the interface have a limited ability to be donors of hydrogen bonds or the localization of EB molecules on the surface prevents the NO_2 groups from binding with water. With the current level of knowledge on water/organic liquids interfaces it is difficult to decide which of these hypotheses is true. Actually, there are arguments against both of them. First, studies of water/carbon tetrachloride interfaces with NMMA probe have shown that molecules of NMMA adsorbed at the interface are strongly hydrogen-bonded with water[15], therefore one should expect that the same is true for EB. On the other hand, one should also expect that the NO_2 groups are submerged in water due to the polar and ionic character of this molecular moiety and strong multiple hydrogen bonds of the NO_2 groups with water should stabilize molecules in this orientation. Thus, there might be an alternative reason for the observed effects: maybe EB molecules are hydrogen-bonded with water, but the energy transfer mechanism is inactive at the interface. The exact mechanism of hydrogen bonds-assisted energy transfer is not known, therefore it is currently impossible to verify this supposition.

Molecular dynamics simulations, similar to those performed for water/glycerol mixtures at the boundary with dodecane, could be very helpful here. They were used for solving a similar problem in the group of G. Richmond where SSFG studies of water/carbon tetrachloride interfaces showed a lack of strong hydrogen bonds[46,47] but simulations carried out a few years later suggested the contrary: a large number of water molecules at the interfaces are strongly hydrogen-bonded, but their orientation – parallel to the interface – makes them undetectable by SSFG measurements[48,49]. This example shows that one has to be very careful when interpreting results obtained by the techniques discussed here. That is why we did not give a single explanation of the observed effects. Still, it is worth to emphasize their potential consequences: the excited state lifetime of eosin B, extremely short (picosecond) in an aqueous environment, can be extended to nanoseconds after EB is adsorbed at a water/nonpolar liquid interface. Such interfaces are present in living organisms, where a polar interior of each cell is surrounded by a nonpolar lipid membrane. Thus, the deactivation mechanism involving hydrogen bonding can make molecules adsorbed on cellular membranes distinguishable by fluorescence imaging. If such an effect really takes place in living organism, a dye such as EB could be used as a fluorescence marker, whose fluorescence yield strongly increases after adsorption on a cell membrane.

The next article [**H5**] presents results of experiments carried out after I left the group of prof. Vauthey. They are an extension of our works on application of probe molecules for detection of ions on surfaces and use experimental apparatus built by Marina Fedoseeva, based on tuneable pulsed laser sources. In this study both cationic (malachite green) and anionic (eosin B) dyes were used as probe molecules, therefore anions as well as cations could be detected at investigated interfaces. Two independent experimental setups allowed measurements of the dependence of second harmonic generation yield on probe wavelength and TRSSHG measurements with the pump and probe beams tuned independently. This greatly enhanced our experimental capabilities, compared to what we had to our disposition previously. For instance, it became possible – by comparing spectra recorded at an interface and in a bulk solution - to unequivocally confirm that second harmonic signals recorded at low malachite green concentrations come from the monomeric form of the dye (Fig. 1 in [**H5**]). Tuning the probe beam, in turn, allowed selective probing of aggregates (at a wavelength where monomers were practically non-resonant) and confirming that they are indeed responsible for the slow component of decays of TRSSHG signals (Fig. 3. in [**H5**]).

The new experimental apparatus also allowed reproducible measurements of the intensity of second harmonic light generated in different samples under different conditions. This ability and the knowledge gained during our earlier works allowed explanation of an effect which I observed already in the beginnings of my studies of interfaces. This effect was expressed through a non-monotonic dependence of the excited state deactivation rate of malachite green on a concentration of a surfactant (sodium dodecylsulfate, SDS) added to the aqueous phase of the water/dodecane interfacial system. At low SDS concentrations the decays of TRSSHG signals became slower when the surfactant concentration increased but upon further addition of SDS they shortened back and finally became as short as without any surfactant. Measurements of the second harmonic intensity carried out in the same conditions showed similar features (Fig. 6 in [**H5**]): with increasing concentration of SDS the second harmonic intensity initially grew up and subsequently dropped down. Whereas the explanation of the non-monotonic changes of the excited state decay rates was difficult for us at the time of the first observation of this phenomenon, it turned out to be relatively simple after carrying out all the works described above and with application of the new experimental equipment.

SDS is a surface active compound, consisting of a polar, negatively charged "head" and a non-polar, linear carbon chain (Fig. 7a). In a system compromised of water and alkane SDS molecules are strongly adsorbed at the phase boundary in such a way that the polar head is submerged in water and the carbon chain protrudes into the organic phase. Presence of a small amount of SDS in the aqueous phase results in an increase of the surface concentration of MG due to electrostatic attraction between the negatively charged heads of adsorbed SDS molecules and MG cations. Consequently, this leads to a slowdown of TRSSHG decays caused by aggregation of adsorbed MG molecules at the interface. After more surfactant is added to the system it displaces MG molecules from the interface because SDS is much more surface-active and the surface concentration of MG drops down. Thus, the described effect results from two phenomena occurring simultaneously in the studied system: electrostatic attraction of dye cations to adsorbed anions of the surfactant and competitive adsorption of the dye and the surfactant, leading to displacement of MG by SDS. The same effect was observed for an oppositely charged dye-surfactant pair, EB anion and cetyl trimethylammonium (CTAB) cation (Fig. 7b).

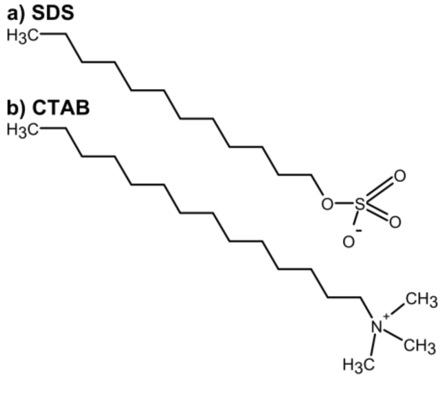


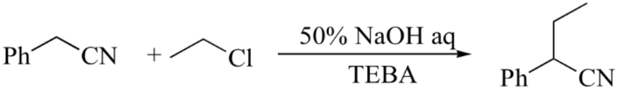
Fig. 7. Structural formula of surfactants used in [**H5**]: a) anionic (SDS); b) cationic (CTAB).

Addition of a surface active ion of the same charge as the probe dye ion results, as expected, in a significant decrease of the surface concentration of the dye due to electrostatic repulsion. Thus, we have shown in this work that surface concentration of organic ions which are weakly surface-active can be controlled by adding a small amount of strongly surface active ionic compounds to the system. This might be utilized for controlling chemical reactions or biochemical processes. On the other hand, surface activity of various ions can be compared by measurements of second harmonic intensity or excited state deactivation rate with an appropriately selected probe dye. In this case it is not necessary to tune the probe beam to electronic transitions of studied ions and the influence of their different hyperpolarization is eliminated.

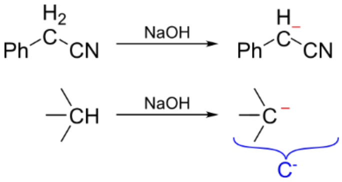
Publications [**H1**-**H5**], like the vast majority of studies of surfaces and interfaces using SSHG, SSFG and related techniques, focus on surface properties in steady state (macroscopically) systems. These techniques, however, have also a high potential for studying dynamic processes such as chemical reactions. Actually, key processes of heterogenic reactions take place at interfaces, therefore techniques capable of detecting and measuring concentrations of selected species (substrates, products or intermediate forms) can be utilized for identification of reactions mechanisms and optimization of their conditions. Unfortunately, not much attention has been paid to this issue so far and studies of intermolecular processes in biphasic systems were limited to interfacial electron transfer[31]. For this reason, after I had finished the postdoctoral fellowship and returned to the University of Warsaw, I started working on applications of SSHG at interfaces for studying heterogeneous chemical reactions. The main result of these studies is the first demonstration of using SSHG for identification of the microscopic mechanism of phase transfer catalysis[50–52] (PTC) [**H6**]. This work was inspired by prof. M. Mąkosza, one of the inventors of this technique of chemical synthesis[53,54].

PTC is a technique of chemical synthesis with reactants located in two non-mixing phases (usually an aqueous phase and a nonpolar organic one, but also a liquid and a solid), which cannot be easily dissolved in the same environment, due to their very different properties. The simplest example of PTC are reactions in which an anion coming from an inorganic salt dissolved in water should react with a non-polar molecule located in an organic phase. In order to transfer this anion into the organic phase, where the desired reaction takes place, a catalyst well soluble in the organic phase and capable of binding with the inorganic anion is added to the system. Such catalysts are typically organic salts of the general formula Q^+X^-, where X is a halide (chloride, bromide…) and the organic cation Q^+ satisfies two conditions: it is strongly lipophilic and can easily make an ion pair with the anion taking part in the reaction. Such a pair is well soluble in the organic phase due to the lipophilicity of the cation Q^+.

In a more complicated case, the anion taking part in the reaction is not directly introduced to the system in the form of a salt as described above, but it is created in the system from an appropriate precursor in the presence of a strong base (such as a saturated aqueous solution of sodium hydroxide NaOH). The first patented (in 1960) reaction based on this concept was a synthesis of 2-phenylbutyronitrile via the reaction of 2-phenylacetonitrile with ethyl chloride. These substrates react only in presence of a saturated NaOH solution and a phase transfer catalyst (such as benzyltriethylammonium chloride, TEBA), even if they are in the same organic phase:



There are two possible explanations of the role of NaOH and the catalyst in this reaction. In the first potential mechanism, interfacial (proposed by prof. M. Mąkosza), phenylacetonitrile is deprotonated by NaOH and its carbanion (further denoted as C^-) is formed on the boundary between NaOH and the organic phase:



The carbanion cannot leave the interface and move to the organic phase (Fig. 8a), because it forms an ion pair with a sodium atom which is strongly solvated in the aqueous environment and very weakly in the non-polar one. Only after the ion exchange reaction with the catalyst Q^+Cl^- an ion pair Q^+C^- is formed and, due to the lipophilicity of the cation Q^+, the carbanion of phenylacetonitrile (C^-) is transferred to the organic phase, where it reacts with ethyl chloride (Fig. 8b).

The alternative mechanism (extraction) was proposed by C. M. Starks[55]. According to this model, first the catalyst Q^+Cl^- undergoes an ion exchange with NaOH. This reaction leads to formation of a hydroxide compromising the catalyst cation, Q^+OH^-. This lipophilic hydroxide migrates into the organic phase and its presence there results in deprotonation of phenylacetonitrile and creation of its carbanion, however not at the interface, as in the mechanism of prof. Mąkosza, but only in the organic phase[52]. This model also involves a situation, in which the hydroxide Q^+OH^- cannot leave the interface, either (Fig. 9a), but it is necessary as an intermediate product for creation of the carbanion because the latter is not formed in a direct reaction with NaOH[56] (Fig. 9b).

Studies of the microscopic mechanism of PTC carried out so far were based on sampling the organic phase of the system and comparing yields of chemical reactions in different conditions. Their results indicated that the interfacial mechanism predominated but did not rule out the extraction mechanism. However, these studies were based on indirect measurements which did not provide direct information on processes at the interface.

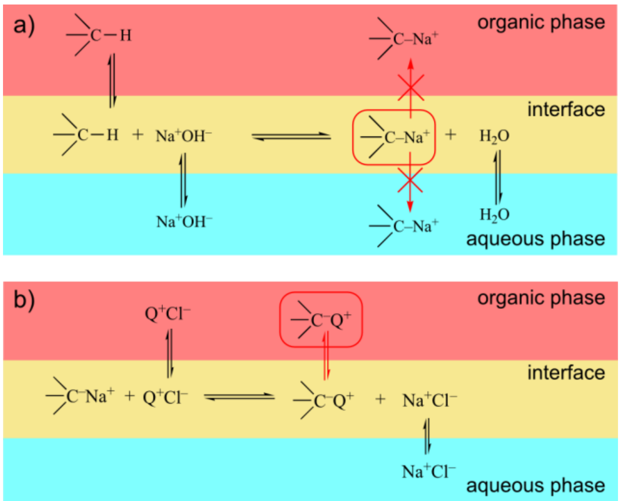


Fig. 8. The interfacial mechanism of phase transfer catalysis: a) without a catalyst; b) after addition of a catalyst to the system.

Therefore, SSHG measurements could help to answer the question of which mechanism predominates in PTC, due to the capability of detecting and measuring surface concentration of various species. The main differences between the mechanisms, which can be easily detected by measuring surface concentration of carbanions are the following:

- in the interfacial mechanism the carbanion is formed at the interface even without a catalyst, whereas in the extraction mechanism only in the presence of a catalyst,
- in the interfacial mechanism addition of a catalyst should lead to the decrease of the surface concentration of carbanions and in the extraction mechanism – to its increase.

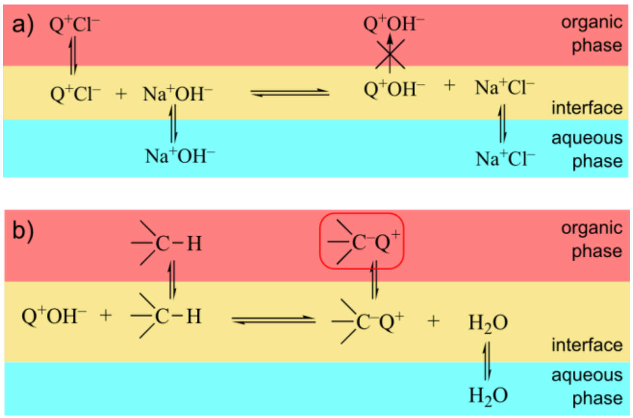


Fig. 9. Extraction mechanism of phase transfer catalysis: a) Formation of a hydroxide compromising the catalyst cation; b) Formation of the carbanion.

This means that one can identify the active mechanism by carrying out SSHG measurements with the probe beam tuned to one- or two-photon transitions in carbanions but not in their precursors. In order to demonstrate that the occurrence of the interfacial mechanism can be proved by such an experiment, I proposed carrying out measurements in a biphasic model system, compromised of a saturated aqueous NaOH solution and an organic phase containing a pH indicator. pH indicators are molecules which are easily deprotonated in a basic environment, thus one can expect that they will efficiently form anions at the interface with NaOH even without a catalyst. Additionally, the change of their form from neutral to anionic is accompanied by a change of their colour because the absorption spectrum of the anion and its precursor differ significantly. This allows selective tuning of the probe beam to one of the forms.

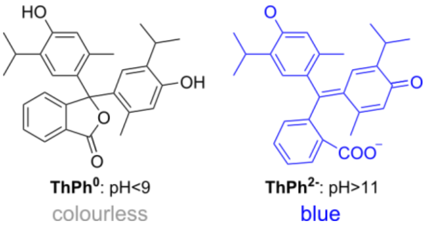


Fig. 10. Neutral and doubly anionic forms of thymolphthalein.

One of pH indicators selected for the described experiments was thymolphtalein (ThPh, Fig. 10). This compound is colourless in organic solvents and in water at low pH, where it is present as a neutral form (**ThPh^0**). In basic aqueous solutions it becomes intensely blue, which results from strong absorption of the doubly anionic form (**ThPh^{2-}**) in the visible range of the spectrum.

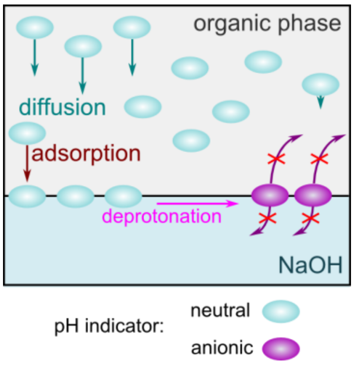


Fig. 11. Scheme of formation and accumulation at the interface of the anionic form of the pH indicator in the model system.

Measurements of how the second harmonic intensity changes in time elapsed after pouring the organic phase containing ThPh on the saturated aqueous NaOH solution (Fig. 3 in [**H6**]) lead to the following description of processes occurring in the system (Fig. 11): neutral molecules **ThPh^0** adsorbed at the interface are deprotonated as a result of interaction with NaOH and the anionic form **ThPh^{2-}** is formed. The latter, in contrast to the neutral form, cannot leave the interface and the equilibrium between the molecules at the interface and in adjacent layers is upset. Concentration of **ThPh^0** near the interface drops down locally, which stimulates the diffusional transport of molecules in solution towards the surface. Subsequently, these molecules are adsorbed and deprotonated. Thus, the surface concentration of **ThPh^{2-}** grows up until the interface is saturated or there is no more ThPh in the bulk solution. This behaviour of the system corresponds well to the interfacial mechanism of anions formation. A simple mathematical model based on the presented interpretation was also proposed because even though there are many models of adsorption described in the literature[57], almost all of them assume equilibrium between the surface and the adjacent layer of the liquid, which is not the case in the discussed experiments. In spite of its simplicity, the model satisfactorily reproduces experimental data and obtained values of parameters match expected values.

The experiments discussed above confirmed that SSHG can be used to observe anions formation on the surface of NaOH solution but they did not involve the process of catalytic transport. This, however, can be easily provoked by adding a phase transfer catalyst to the system – its addition leads to fast coloration of the organic phase due to the appearance of characteristic bands of **ThPh^{2-}** in the absorption spectrum of the organic phase (Fig. 5 in [**H6**]). Addition of the phase transfer catalyst to the organic phase also induces a fast decrease of the second harmonic intensity due to the transfer of anions (in pairs with cations of the catalyst) from the interface to the solution (Fig. 12).

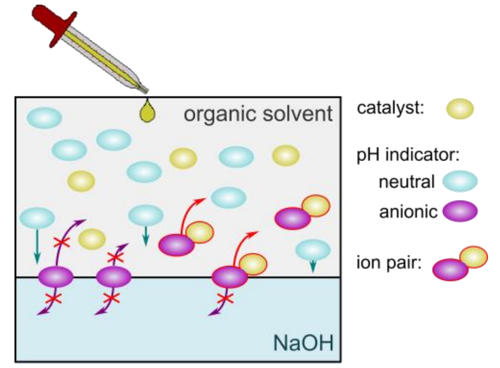


Fig. 12. Scheme of processes in the model system occurring after addition of a phase transfer catalyst.

All the above observations correspond to the interfacial mechanism of PTC. It is also known that due to the properties of the pH indicators used in the model system, formation and transport of the anions should follow this mechanism. It has been, therefore, confirmed that SSHG can be used for identification of the microscopic mechanism of phase transfer catalysis.

These results created a basis for studies of formation of carbanions, in case of which the hydrogen atom is removed from a carbon atom of their precursors, as in real PTC systems. Here, the deprotonation of a carbon atom does not occur as easily as in case of pH indicators. Preliminary experiments showed that the behavior of such systems was different than that of the model system: the surface concentration of carbanions was low (but non-zero) without a catalyst and significantly increased after addition of a catalyst. This indicated that the catalyst played a role in the deprotonation process. However, surface concentration of carbanions decreased with the increase of the lipophilicity of the catalyst, which means that the catalyst also facilitates the transport of carbanions from the interface to the solution. These results show that the interfacial mechanism plays a role in the studied systems because certain amount of carbanions is formed without a catalyst. At the same time, however, it can be stated that the catalyst is also involved in the formation of carbanions and not only in their transport. These experiments, which were the basis of the bachelor's thesis of Michał Hamkało[58] prepared under my supervision, point to an interesting direction of future research.

In the series of articles [**H1**-**H6**] applications of techniques based on the second harmonic generation of light for studies of physicochemical properties of interfaces and phenomena occurring on phase boundaries were demonstrated. These works started from attempts to study the influence of properties of liquids on parameters and processes such as microscopic viscosity and rotations at interfaces [**H1**]. Subsequently, they were aimed at applications of SSHG for studying processes involving more than one molecule. It seems that the greatest research potential of the discussed techniques lies in their applications to study chemical reactions involving molecules adsorbed at interfaces or located in different phases. An appropriate example was demonstrated in the publication [**H6**], opening a way towards direct studies of the microscopic mechanism of phase transfer catalysis, a class of heterogeneous reactions with a significant impact on the chemical industry.

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5. Description of remaining achievements in science and research

a) before receiving the PhD degree

I had the first contact with research work when I was still a high school student, by taking part in workshops organized by the Polish Children's Fund in the Institute of Physics, Polish Academy of Sciences. During the workshops I was involved in the research in the field of condensed matter physics [**A14**]. Shortly afterwards I took part in the Research Science Institute organized at the MIT, working in the Phobos collaboration. The collaboration was building one of the detectors at the Relativistic Heavy Ion Collider (RHIC) and my task was to build a device for automated testing of detector's elements. I continued this collaboration and I was involved in creation of the software and user interface for the slow control of the detector. As a collaborator I was a co-author of first publications reporting results obtained with the PHOBOS detector [**A10**-**A13**] but because of my relatively small contribution, I do not take these publication into account when calculating indices of scientific achievements, such as the total impact factor, Hirsch index or the total number of citations.

I started the regular scientific work in the field of optics while studying at the Faculty of Physics, University of Warsaw, in the group of prof. Czesław Radzewicz. My work was focused on time-resolved spectroscopy of organic molecules in solutions and included the development of emission and absorption spectroscopy techniques with femtosecond temporal resolution. In particular, we demonstrated for the first time the application of parametric amplification of light for gating and amplifying fluorescence [**A9**]. This allowed constructing a relatively simple apparatus which was capable of recording time-gated emission spectrum of organic molecules in the visible range at once. On the other hand, I was using transient absorption techniques for studies of light induced processes in Schiff bases [**A5**, **A7**, **A8**], collaborating with prof. Anna Grabowska from the Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS). As a part of this work I developed an algorithm for the global analysis of spectroscopic data, which is much faster than such procedures used in commercial software. This algorithm is currently used in software written and used by several research groups over the world. Later, I started a collaboration with prof. Jacek Waluk from IPC PAS and I developed a technique of using transient absorption anisotropy measurements for studying the double hydrogen transfer in porphycene and its derivatives [**A1**-**A3**].

b) after receiving the PhD degree

After receiving my PhD I started a postdoctoral fellowship in the group of prof. Eric Vauthey at the Geneva University, where I became involved in the research on the properties of interfaces and processes occurring at phase boundaries. The results of these works are a part of the scientific achievement [**H1**-**H5**, **A18**]. In parallel I continued studies of the double hydrogen transfer in porphycene derivatives, using the equipment available in the group of prof. Vauthey [**A21**, **A24**, **A25**] (also during a 3 months long internship in 2011). I also started a collaboration with the group of prof. Jadwiga Mielcarek from the Poznań University of Medical Sciences, which I continued after coming back from the postdoctoral fellowship. As a result of this collaboration we studied photophysical and photochemical properties of a series of new porphyrinoids synthesized as potential photosensitizers for the photodynamic therapy [**A17**, **A19**, **A22**, **A23**]. Later, while working at the University of Warsaw, I further developed techniques of studying the double hydrogen transfer in porphycenes and designed a new experimental setup for transient absorption anisotropy measurements. Simultaneously, I was working on applications of nonlinear optical spectroscopy at interfaces for studying chemical reactions at phase boundaries [**H6**].

c) Research articles published before receiving the PhD degree

A1. P. Fita, N. Urbańska, C. Radzewicz, J. Waluk , *Ground- and Excited-State Tautomerization Rates in Porphycenes* , Chem. - Eur. J. **15**, 4851 - 4856 (2009).

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A3. P. Fita, N. Urbańska, C. Radzewicz, J. Waluk, *Unusually Slow Intermolecular Proton-Deuteron Exchange in Porphycene*, Z. Phys. Chem. **222**, 1165 - 1173 (2008).

A4. P. Migdał, P. Fita, C. Radzewicz, Ł. Mazurek, *Wavefront sensor with Fresnel zone plates for use in an undergraduate laboratory*, Am. J. Phys. **76**, 229 - 235 (2008).

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A9. P. Fita, Y. Stepanenko, C. Radzewicz, *Femtosecond transient fluorescence spectrometer based on parametric amplification*, Appl. Phys. Lett **86**, 021909 (2005).

A10. B.B. Back et al., *The PHOBOS detector at RHIC*, Nucl. Instrum. Meth. A **499**, 603 – 623 (2003).

A11. R. Pak et al., *The PHOBOS detector at RHIC*, Nucl. Phys. A **698** , 416C - 419C (2002).

A12. E. Garcia et al., *Phobos at RHIC 2000*, Rev. Mex. Fis. **47**, 98 - 103 (2001).

A13. B.B. Back et al., *Charged-particle multiplicity near midrapidity in central Au plus Au collisions at* $\sqrt{s} =$ *56 and 130 GeV*, Phys. Rev. Lett. **85**, 3100 - 3104 (2000).

A14. P. Fita, K. Smoliński, Z. Gołacki, K. Ławniczak-Jabłońska, *X-ray characterization of precipitates in cerium-doped PbTe and SnTe crystals*, Appl. Phys. A - Mater. **68**, 681 - 685 (1999).

d) Research articled published after receiving the PhD degree

A15. P. Ciąćka, P. Fita, A. Listkowski, M. Kijak, S. Nonell, D. Kuzuhara, H. Yamada, C. Radzewicz, J. Waluk, *Tautomerism in Porphycenes: Analysis of Rate-Affecting Factors*, J. Phys. Chem. B **119**, 2292-2301 (2015).

A16. M. Józefowicz, P. Fita, P. Kasprzycki, J. R. Heldt, *Excited-State Dynamics of Ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate*, J. Phys.Chem. A **117**, 4136 - 4147 (2013).

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A23. T. Goslinski, T. Osmalek, K. Konopka, M. Wierzchowski, P. Fita, J. Mielcarek, *Photophysical properties and photocytotoxicity of novel phthalocyanines - potentially useful for their application in photodynamic therapy*, Polyhedron **30**, 1538 - 1546 (2011).

A24. P. Fita, P. Garbacz, M. Nejbauer, C. Radzewicz, J. Waluk, *Ground and Excited State Double Hydrogen Transfer in Symmetric and Asymmetric Potentials: Comparison of 2,7,12,17-Tetra-n-propylporphycene with 9-Acetoxy-2,7,12,17-tetra-n-propylporphycene*, Chem. - Eur. J. **17**, 3672 - 3678 (2011).

A25. M. Gil, J. Dobkowski, G. Wiosna-Sałyga, N. Urbańska, P. Fita, C. Radzewicz, M. Pietraszkiewicz, P. Borowicz, D. Marks, M. Glasbeek, J. Waluk, *Unusual, Solvent Viscosity-Controlled Tautomerism and Photophysics: Meso-Alkylated Porphycenes*, J. Am. Chem. Soc. **132**, 13472 - 13485 (2010).

A26. M. Pawłowska, F. Ozimek, P. Fita, C. Radzewicz, *Collinear interferometer with variable delay for carrier-envelope offset frequency measurement*, Rev. Sci. Instrum. **80**, 083101 (2009).

e) bibliometric indicators

- Total *impact factor* according to the JCR list for the year of publication: 92.375
- Total number of citations according to the Web of Science (WoS): 323
- Citations without self-citations according to the Web of Science: 277
- Hirsch index according to the Web of Science: 12

  (*bibliometric indicators are given without publications [**A10-A13**]*)

Piotr Fita