# Ultrafast Photoinduced Dynamics at Air/Liquid and Liquid/Liquid Interfaces

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ABSTRACT: Although liquid/liquid and air/liquid interfaces are omnipresent, very little is known up to now about the dynamics of processes occurring at such interfaces. As a detailed understanding of these processes could be of invaluable technological, environmental, and medical importance, considerable effort has been invested over the last two decades in developing new interface-selective techniques that allow for gaining further insight into the dynamics of these processes. Whereas several major results have been achieved that helped to contribute to a deeper understanding, there are still many aspects concerning the properties of liquid interfaces that are not yet fully understood. In this Perspective, the work that has been carried out so far on photoinduced interfacial dynamics will be reviewed and the current challenges in this still emerging field of research discussed.
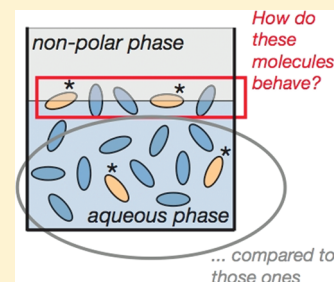
M any processes that we come across in everyday life occur at liquid interfaces (air/liquid and liquid/liquid).[1] Pertinent examples include atmospheric and environmental chemistry, heterogeneous catalysis, as well as photosynthesis or any other type of membrane transfer phenomena or membrane reactions taking place in biological environment.

In order to describe and understand these processes at a molecular level, we need detailed information about the orientation of the molecules, their interaction, their energetics, and the time scale of their motion.

The reason why, despite their evident importance, relatively modest knowledge has been achieved so far about processes occurring at liquid interfaces is certainly connected to the fact that information about interfacial properties is difficult to access. In order to be useful for studying liquid interfaces, the employed technique needs to be somehow interface-selective; otherwise, the response from the small number of interfacial molecules is totally buried in that arising from the molecules in the bulk phases. The optical spectroscopic techniques that have been used up to now for these studies can be categorized into two groups. The first group relies on the confinement of the optical beam(s) close to the interfacial region, using evanescent waves generated upon total internal reflection (TIR) at the interface of two materials with different refractive indices, whereas the second one profits from the inherent lack of even order nonlinear response of isotropic bulk media.

> Information that is straightforward to obtain in bulk solution is much more problematic to obtain at interfaces.

The most popular method based on evanescent waves is time-resolved TIR fluorescence (TR-TIRF, Figure 1A). By combining time-correlated single-photon counting (TCSPC) with laser pulse excitation in TIR geometry, the fluorescence
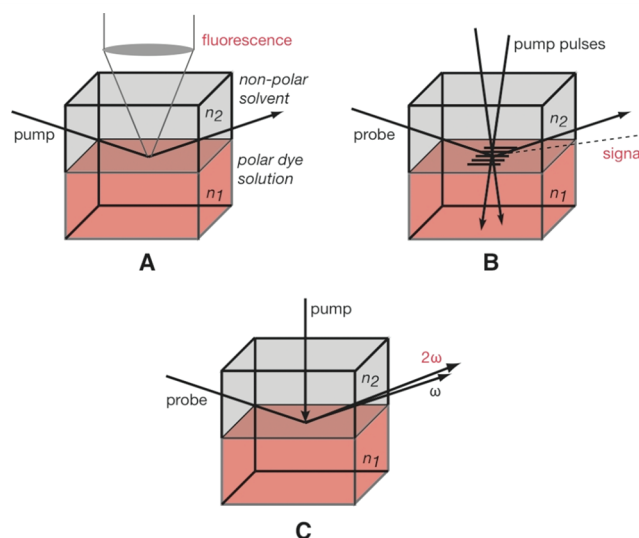

Figure 1. Schematic layouts of the different techniques used for studying liquid interfaces: (A) time-resolved total internal reflection fluorescence (TR-TIRF); (B) transient grating; (C) time-resolved surface second-harmonic generation (TR-SSHG).

lifetime of molecules close to the interface can be measured with a resolution of a few tens of picoseconds. For example, the fluorescence dynamics of coumarin 343 (C343) dissolved in water at the interface with 1,2-dichloroethane (DCE) could be well-reproduced by a biexponential decay, with a 3.6 ns component, close to the lifetime of the dye in bulk water, and a 0.3 ns component ascribed to aggregates.[2] An interesting feature of TIR techniques is the possibility to vary the penetration depth of the evanescent field by changing the angle

of incidence of the laser beam on the interface, allowing the depth profile of a given property to be reconstructed. Nevertheless, it should be noted that the penetration depth is a complex function of the angle of incidence and that, therefore, both the penetration depth as well as the resolution of depth crucially depend on this angle. For example, a small variation (~0.1°) of the angle of incidence near the critical angle can change the penetration depth by several tens of nanometers.

In the case of C343 at the water/DCE interface, the aggregate/monomer ratio was found to substantially decrease upon changing the penetration depth from 95 to 120 nm, showing that aggregates are preferentially present at the interface.[2] By measuring the time dependence of the fluorescence anisotropy upon TIR excitation, information on the reorientational dynamics of the fluorophore close to the interface is rather easily accessible. This was used, for example, to investigate the reorientational dynamics of sulforhodamine 101 in phthalate esters of different viscosity close to the interface with water.[3] Two reorientational times were found and ascribed to different adsorption modes of the probe at the interface. On the other hand, the viscosity dependence of these time constants was consistent with that measured in bulk phthalate ester solutions.

Despite many advantages, notably, its simplicity, TR-TIRF suffers from several limitations. Indeed, it does not yield any access to the dynamics of dark species, and its time resolution is limited to that of the TCSPC technique, that is, around 20 ps.

These restrictions can be circumvented by using time-resolved attenuated TIR (TR-ATIR), where a photoinduced process is triggered in the low refractive index medium by a laser pulse, and the intensity change of a probe beam in TIR geometry is monitored. This technique has been used on the nanosecond to microsecond time scales for determining the triplet state lifetime of a water-soluble porphyrin at the interface with toluene.[4] The faster quenching of the triplet state at the interface compared to that in bulk aqueous solution was ascribed to a more efficient triplet–triplet annihilation or energy transfer due to the higher interfacial concentration of porphyrins. In this case, probing was done with a continuous polychromatic beam, and transient ATIR spectra were recorded. Although the signal intensity is a complex function of the absorption and refractive index spectra of both phases and of the angle of incidence, the main features of transient ATIR spectra can be reasonably well compared with those of a conventional transient absorption spectrum. However, the major drawback of TR-ATIR is its poor sensitivity. In order to produce a detectable TR-ATIR signal, measurable photoinduced changes of absorbance over the penetration depth of the probing evanescent field are required. This is only possible with strongly absorbing molecules or highly concentrated solutions, limiting the number of systems that can be studied, because of solubility or self-quenching. For most studies, it is crucial to keep the dye concentration as low as possible to minimize the perturbations of the interface.

The high sensitivity of TR-TIRF due to the zero-background nature of the signal and the sensitivity of TR-ATIR to dark states are somehow combined in the evanescent transient grating technique. In one of the possible configurations of this four-wave mixing method (Figure 1b), a transient grating generated upon interference between two pump pulses diffracts the probe pulse in TIR geometry. As the intensity of the diffracted signal is directly proportional to the photoinduced changes of the refractive index and absorbance, a large variety

of phenomena, ranging from population dynamics to thermoacoustic effects, can be investigated. For example, the decay of the S_1 state lifetime of rhodamine 6G dissolved in methanol at the interface with decaline was found to be about three times as short as that in bulk methanol solution of the same concentration.[5] This effect was ascribed to self-quenching favored by a higher interfacial concentration of rhodamine compared to bulk. The same technique was also used to measure the speed of sound and the acoustic attenuation in the methanol phase close to the interface with decaline on a picosecond to millisecond time scale.[6] Although more sensitive than TR-ATIR, this evanescent transient grating technique also requires substantial concentration of absorber to realize sufficient modulations of the absorbance and refractive index over the penetration depth of the evanescent field.

The evanescent waves accounting for the interface sensitivity of all of the above-described TIR techniques generally feature a penetration depth of the order of 100 nm. On the other hand, molecular dynamics simulations point to an interfacial thickness typically of 1 nm.[7] Therefore, TIR techniques can only yield true interfacial information if the probe molecules are highly surface active, implying that the concentration of molecules adsorbed at the interface should be at least one order of magnitude larger than their bulk concentration. As this is only the case for a small number of molecules, this requirement represents a severe limitation to the applicability of all of the above-mentioned TIR techniques for investigating excited-state dynamics at liquid interfaces.
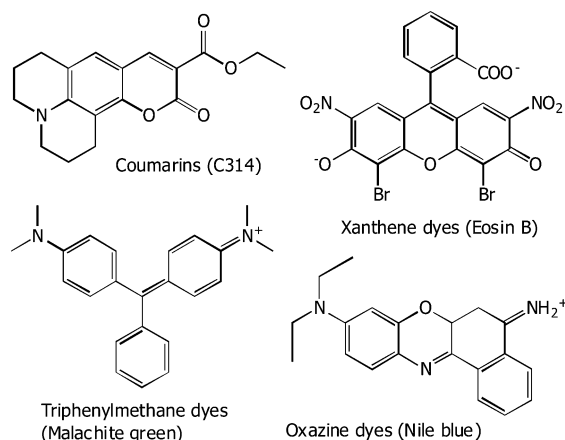
Even-order nonlinear optical phenomena offer the remarkable advantage that they are electric-dipole-forbidden in centrosymmetric molecules and bulk materials. Indeed, molecules with a center of inversion have zero even-order hyperpolarizability. Furthermore, a bulk material composed of randomly oriented asymmetric molecules has also zero even-order nonlinear optical susceptibility, $\chi^{(2n)}$, because the even-order responses from the individual molecules are canceled by destructive interference. On the other hand, the interface between two bulk materials is not centrosymmetric and, because of the asymmetry of forces, it has a nonvanishing $\chi^{(2n)}$. This asymmetry of forces can be strong enough to distort centrosymmetric molecules, resulting in a nonvanishing hyperpolarizability.[8] This makes even-order nonlinear spectroscopic techniques truly interface-selective.

Due to their selectivity and simplicity relative to higher even-order methods, time-resolved second-order nonlinear techniques, like surface second-harmonic generation (TR-SSHG) and sum frequency generation (TR-SSFG), have been the methods of choice for studying dynamic processes at liquid interfaces over the past ~20 years. An additional important feature of these techniques arises from the frequency dependence of the second-order nonlinear susceptibility, $\chi^{(2)}$, that exhibits resonances at frequencies corresponding to one- and two-photon transitions of the material. As a consequence, if in a SSHG experiment, the frequencies of the probe and/or SSHG fields coincide with an electronic transition of a molecule dissolved in one of the phases constituting the interface, the SSHG signal from these solutes is strongly resonantly enhanced relative to that from the solvent molecules. Owing to electronic resonance enhancement, interfacial spectroscopy can be performed with solute molecules at relatively low bulk concentration (~10^{-5} M). This feature is fundamental for TR-SSHG, where the solute molecules are first photoexcited by a pump pulse, and only those at the interface are probed by

SSHG (Figure 1c). TR-SSFG can be performed upon either electronic (vis-pump),[9] or vibrational (IR-pump)[10−12] excitation. Although well-suited for studying interfacial properties, IR-pump TR-SSFG spectroscopy does not yield direct information on the excited-state dynamics of dye molecules adsorbed at the interface. In the following, we will therefore only focus on electronic TR-SSHG and TR-SSFG and describe their most relevant applications for investigating the dynamics of photoinduced phenomena at liquid interfaces. We shall also discuss the limitations of the currently used experimental setups and identify the problems concerning data analysis and interpretation that we are presently facing in this fascinating but challenging research area.

Studies on interfacial dynamics by second-order nonlinear techniques were pioneered by Eisenthal and co-workers.[13,14] Since about 20 years, his group and others have applied TR-SSHG as well as vibrational[15−17] and electronic[18,19] TR-SSFG to investigate the dynamic behavior of various molecules (cf. Chart 1) at air/liquid or liquid/liquid interfaces. In most cases,

Chart 1. Representative Selection of Molecules Used As Interfacial Probes

Coumarins (C314)

Xanthene dyes (Eosin B)

Triphenylmethane dyes
(Malachite green)

Oxazine dyes (Nile blue)

the results obtained at an interface have subsequently been compared to the corresponding bulk behavior of the molecule, and the differences in the observed dynamics were attributed to the specific interfacial properties.

Solvent is well-known to play a crucial role in chemistry, acting as a heat bath that can transfer energy to the reactants or absorb the energy dissipated by the reaction and influencing the relative energies of the reaction educts, intermediates, and products. Understanding solvent motion at interfaces is thus of paramount importance for a comprehensive picture of interfacial chemistry. Studying solvation dynamics in bulk solution is relatively straightforward. Solvent relaxation around a photoexcited molecular probe results in a dynamic Stokes shift of the emission spectrum that can be measured, for example, by femtosecond time-resolved fluorescence and analyzed using well-established procedures (Figure 2).[20] One approach to access solvation dynamics by TR-SSHG is to assume that the second-order nonlinear susceptibility, $\chi^{(2)}$, has only contributions from $S_1 \leftarrow S_0$ and $S_1 \rightarrow S_0$ resonances and that, because of solvent relaxation, the latter depends on time after excitation (cf. Figure 2).[21] A series of measurements of $\chi^{(2)}$ as a function of time and wavelength should thus allow reconstructing the whole TR-SSHG spectrum, and the solvation dynamics could then be obtained in a similar way
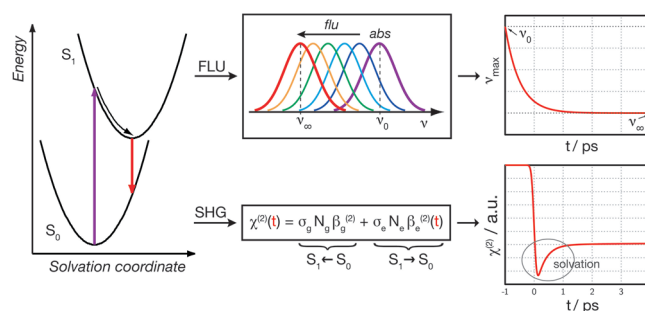

Figure 2. Effect of solvent relaxation on the fluorescence spectrum (top) and second-order nonlinear susceptibility (bottom).

as in bulk solution, that is, by monitoring the position of the SSHG band maximum as a function of time. However, this method is highly time-consuming and requires a tunable probe pulse. This procedure can be simplified by probing at a wavelength where the time dependence of the signal intensity is linear with the solvation-induced shift of the whole band. In the case of fluorescence, these wavelengths can be identified by recording the emission spectrum in solvents of different polarity.[22] The solvation dynamics of C314 at the air/water interface has been measured using TR-SSHG assuming that the optimal probe wavelength is the same as that for the fluorescence Stokes shift.[21] As the solvation time measured at the interface, ∼800 fs, was similar to that of diffusional motion in bulk water, it was concluded that the water−water interactions are similar in both cases. Furthermore, these results were compared with those obtained at air/water interfaces in the presence of different concentrations of a neutral,[23] anionic,[24] and cationic[25] surfactant. Addition of a neutral surfactant, stearic acid, at the air/water interface was found to accelerate solvation of C314 by a factor of about two. This was attributed to a rearrangement of the hydrogen-bond network upon interaction with the hydrophilic head of stearic acid. On the other hand, a negatively charged surfactant (stearate) was found to make solvation about twice as slow as that without surfactant, that is, four times slower than that with a neutral surfactant. This effect was ascribed to an increased hydrogen-bonding order and thus a loss in diffusional mobility due to the strong electrostatic field generated by the negative charges at the interface. Finally, the dynamics measured with a cationic surfactant (dodecyl trimethylammonium bromide, DTAB) is between that found with a neutral surfactant and that measured at a neat air/water interface. This was explained by opposite orientations of the water molecules close to the surfactant layer and of the C314 probe molecule due to the opposite charge, leading to different specific interactions.

Although being very useful for getting qualitative information on interfacial solvent motion, this approach relies on the assumptions that (1) C314 behaves as a two-level system at the probe wavelength and (2) the shape and solvent dependence of the SSHG spectrum is the same as that for the fluorescence spectrum. The current status of nonlinear interfacial spectroscopy does not allow either of these assumptions to be confirmed or rejected. Thus, a quantitative knowledge of interfacial solvation dynamics is still not available, although this goal does not appear beyond reach.

Valuable information on the local environment of a molecule, such as viscosity, solute−solvent interactions, or spatial confinement, can be obtained by investigating its reorientional dynamics. In bulk solution, such studies are routinely carried

out by performing polarization-dependent fluorescence or pump–probe measurements, where polarization components of the signal parallel and perpendicular to that of the excitation field are measured and combined to calculate the anisotropy. In principle, a similar approach can be used in TR-SSHG or TR-SSFG, but it is complicated by the fact that the signal is due to a second-order polarization that depends on the interaction of two electric fields with the sample and not a single one like in fluorescence. Moreover, whereas reorientational motion in bulk solution can in most cases be well described with a single time constant, in-plane and out-of-plane motion have to be distinguished at interfaces (Figure 3). This has been
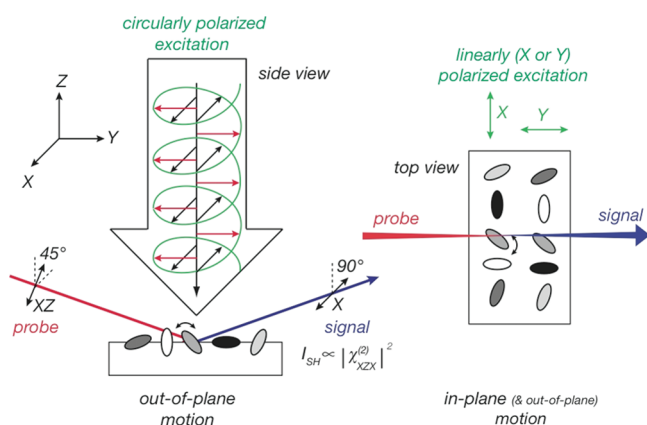

Figure 3. Measurement of out-of-plane (left) and in-plane (left) orientational motions at a liquid interface. The gray scale reflects the probability of a dye to interact with the pump light.

demonstrated by performing TR-SSHG on C314 at the air/water interface.[26] Out-of-plane motion was selectively measured using a pump pulse with circular polarization and by probing the $\chi^{(2)}_{XZX}$ tensor element. This is done by using a probe field polarized at 45° relative to the plane of incidence (Figure 3), thus having components along X and Z, and detecting the X component of the signal. On the other hand, the signal obtained by probing the same tensor element but with a pump pulse polarized linearly along X or Y is sensitive to both in-plane and out-of-plane motions. The in-plane reorientation time can be disentangled by assuming that the time-dependent ground- and excited-state distributions are separable in in-plane and out-of-plane angles and that the out-of-plane component is identical for both X and Y pumping.

In-plane reorientation was found to be slower than the out-of-plane motion with time constants of about 600 and 350 ps, respectively. This is substantially slower than the reorientational time of ~100 ps measured in bulk water with coumarins of similar hydrodynamic volume.

The effect of the addition of a negatively charged surfactant, sodium dodecylsulfate, on the out-of-plane,[15,27] and in-plane,[28] reorientational dynamics of C314 at the air/water interface has subsequently been investigated. The out-of-plane motion was measured by both electronic TR-SSHG[27] and vibrational TR-SSFG. In the latter case, the carbonyl stretching mode of C314 was monitored.[15] The reorientational time constant obtained from TR-SSFG was found to be smaller by a factor of 1.5 compared to TR-SSHG. This was explained by the fact that these two experiments do not probe the same resonance, and thus, rotational motion around different molecular axes is measured. Surprisingly, the presence of SDS was found to have

little effect on the reorientational dynamics of C314, although substantial changes of the orientation of the dye were noticed. More recently, Fayer and co-workers have derived analytical expressions of the orientational correlation functions probed in resonant TR-SSHG and TR-SSFG experiments.[29] By applying the wobble-in-a-cone model to evaluate the correlation functions, this theoretical investigation revealed that the measured decay of the TR-SSHG signal does not directly reflect the reorientational relaxation at the interface. In fact, the observed decay time strongly depends on the angular distribution of the probe molecules at the interface, and as a consequence, the interfacial reorientation time can only be obtained from the measured data provided that this angular distribution is known. When applying this theory to the experimental C314 data, it appeared that the reorientational time constant of C314 at the air/water interface is smaller than that in the bulk by a factor of about 2.5, as originally concluded, but that the addition of SDS slows down the reorientation diffusion by a factor of 3, in contrast to the previous conclusions based on the assumption that the measured decay directly reflects reorientational relaxation. This is an exemplary illustration of how information that is straightforward to obtain in bulk solution is much more problematic to obtain at interfaces. An additional problem is that the contribution of reorientation relaxation to the measured TR-SSHG time profile may, in some cases, be difficult to distinguish from those due to solvation and population changes, unless their time scales are sufficiently different. This difficulty could be partially alleviated by measuring different tensor elements of $\chi^{(2)}$ by varying the polarization of the pump, probe, and signal fields. Finally, if the interfacial concentration of probe molecules is high, the hopping of the excitation energy between nearby molecules might be wrongly interpreted as diffusional reorientation.[30]

Although this might not be as evident as solvent and orientation relaxation, the excited-state dynamics of a well-chosen probe can also yield precious information on its local environment. For example, the dynamics of nonradiative deactivation processes involving an intramolecular coordinate with large-amplitude motion is very sensitive to local friction, and in bulk solution, the viscosity dependence of the measured decay time can be expressed as $\tau_{nr} \propto \eta^{\alpha}$, where α varies between 0.1 and 1 depending on the molecule.[31] Thus, the excited-state lifetime of such molecules at liquid interfaces gives access to the local friction. Measuring population dynamics in bulk solution is generally carried out using time-resolved fluorescence or transient absorption, and to avoid contribution from reorientational motion to the dynamics, the signal is detected at magic angle. When working on the femto- and picosecond time scales, solvent and vibrational relaxations also take place in parallel to population relaxation and lead to spectral dynamics. To identify these various processes, one usually performs a global analysis of time profiles recorded at several wavelengths and compares the so-obtained decay-associated spectra. The situation is more complex at interfaces as TR-SSHG is usually performed at a single wavelength, and therefore, the interpretation of the signal may, in some cases, be ambiguous. For example, the SSHG intensity probed in resonance with the $S_1 \leftarrow S_0$ transition of a series of oxazines at the air/water interface upon excitation to the S_1 state was found to decrease at time zero and to increase biexponentially to almost its original value with time constants around 5 and 25 ps.[32] This fast recovery of the SSHG signal was assigned to the

repopulation of the ground state of the oxazines in H-aggregate form, with the fast and slow components ascribed to solvation and vibrational cooling of the ground state, respectively.

Along the same line, the TR-SSHG profile measured upon $S_1 \leftarrow S_0$ excitation of malachite green (MG) at air/water and alkane/water interfaces and with the SHG signal at 400 nm in resonance with the $S_2 \leftarrow S_0$ transition was also found to increase biexponentially to its original value.[19,33−35] Whereas the fastest component of 1−2 ps has been generally ascribed to the nonradiative transition from the S_1 state, the origin of the slower component, around 20 ps, was much less clear. The increase of the amplitude of this slow component at alkane/ water interfaces with increasing MG concentration was a strong indication that it is due to the nonradiative deactivation of aggregates, at least at these interfaces.[35] This interpretation was further confirmed by the observation that the amplitude of this slow component also increases upon addition of sodium salts to the aqueous phase by an amount that depends on the anion. The effect was found to be moderate with the chloride anion and large with the thiocyanate anion.[36] This salt effect, also observed at the air/water interface,[34] was explained in terms of the Hofmeister series for anions according their salting-in/ salting-out properties.[36] SCN^- is used as a denaturant of proteins because of its affinity to oil/water interfaces. This interface affinity causes a higher interfacial concentration of this anion relative to the bulk, which results in a globally negatively charged interface, favoring the adsorption of the cationic MG molecules and thus aggregation. In this way, TR-SSHG can be advantageously used to determine the relative affinity of ions for interfaces.

Whereas the nonradiative decay time of the S_1 state of MG via large-amplitude motion is around 1−2 ps at air/water and alkane/water interfaces, it amounts to 500 fs in bulk water, indicating that the specific structure of interfacial water results in a larger friction. Increasing the viscosity of the aqueous phase upon addition of glycerol caused a slow down of the nonradiative decay. However, it was found that this effect is more marked in bulk water−glycerol mixtures with $\tau_{nr} \propto \eta^{0.6}$ than at the interface with dodecane, where $\tau_{nr} \propto \eta^{0.4}$.[35] The origin of this difference is still not fully understood but might arise from different compositions of the water−glycerol mixtures in the bulk and at the interface.

The idea of changing the viscosity of the aqueous and nonaqueous phases has been exploited to identify the intramolecular coordinate responsible for the nonradiative relaxation of the S_1 state of two hemicyanines.[37] The viscosity of both phases was systematically varied, and the S_1 lifetime measured at the interface was found to be only influenced by the viscosity of the apolar phase but not by that of the polar phase (Figure 4). This allowed the authors to conclude that the nonradiative deactivation of the excited state of these hemicyanines is driven by large-amplitude motion in their hydrophobic part. This is a promising application of interfaces for mechanistic studies that is much less costly than the usual procedure that consists of the synthesis of derivatives with bulky groups hindering motion along specific coordinates.

Hydrogen-bonding to solvent molecules is also known to favor, in some cases, the nonradiative relaxation of excited molecules. Although the exact mechanism underlying this process is still not fully understood, it can shorten the excited-state lifetime of molecules containing, for example, carbonyl or nitro groups down to a few tens of picoseconds in water. This is the case of eosin B, whose S_1 lifetime in water has been recently
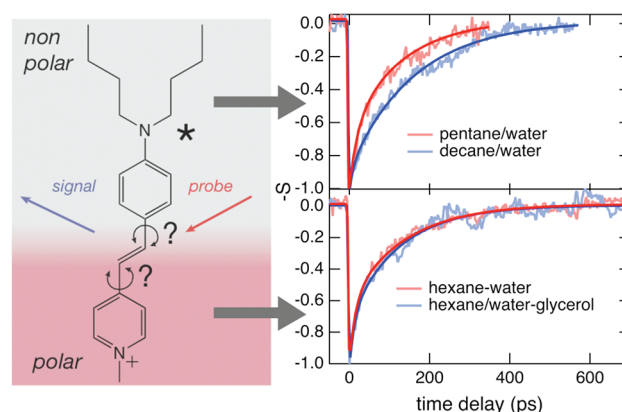

Figure 4. Effect of the variation of viscosity of nonpolar and polar phases on the excited-state lifetime of a hemicyanine at a liquid interface. The reported signal, S, corresponds to the intensity-normalized variation of the square root of the SSHG intensity.

measured to be as short as 4 ps.[38] The determination of the excited-state lifetime of eosin B at alkane/water interfaces was complicated by the formation of aggregates, which leads to a acceleration of the TR-SSHG decay with increasing dye concentration.[39] Despite this effect, the measured lifetime at the interfaces was still much longer than that in the bulk, revealing that hydrogen-bond-assisted nonradiative deactivation is no longer operative at the interface. However, the exact reason for this, for example, an unfavorable orientation of the molecule or a reduced hydrogen-bond-donating ability of interfacial water, could not be clearly established.

All of the phenomena discussed so far are photophysical rather than photochemical processes. The investigations of the dynamics of truly photochemical reactions at the liquid interface are still extremely scarce. One breakthrough in this direction was the TR-SSHG study of the electron-transfer (ET) quenching of C314 by N,N-dimethylaniline (DMA) at the water/DMA interface.[40] As the donor is a molecule of the solvent constituting the hydrophobic phase, this bimolecular ET does not require any translational diffusion of the reactants to take place. Probing upon photoexcitation of C314 was first performed in resonance with the $S_1 \leftarrow S_0$ transition of C314. A biphasic time profile was observed with time constants around 400 fs and 14 ps and ascribed to solvent relaxation and ET quenching of C314, respectively. To confirm this, probing was then carried out in resonance with the $D_1 \leftarrow D_0$ transition of the DMA$^{\bullet+}$ radical cation. In this case, the TR-SSHG signal intensity was found to first rise with a time constant close to the quenching time of C314 and then to decay with a 160 ps time constant. The rise was thus ascribed to the build up of the DMA$^{\bullet+}$ population by ET, whereas the decay was interpreted as the geminate recombination of the ion pair population. Unfortunately, no direct comparison with the same reaction in the bulk, neither in pure DMA nor in acetonitrile/DMA mixtures, was performed.

Although this overview of investigations on ultrafast photoinduced processes at liquid interfaces does not pretend to be exhaustive, it gives a general idea of the present status in this field. Clearly, only a few trails have been explored so far, and our general knowledge is still lacunary. There are several reasons for this. One of them is that the experimental tools used up to now are still relatively primitive compared to the level of sophistication of the spectroscopic techniques applied for studying photoinduced processes in bulk solution. Indeed,

all of the experimental studies presented so far on air/liquid and liquid/liquid interfaces make use of very similar setups. A typical TR-SSHG setup is depicted in Figure 5 and will be
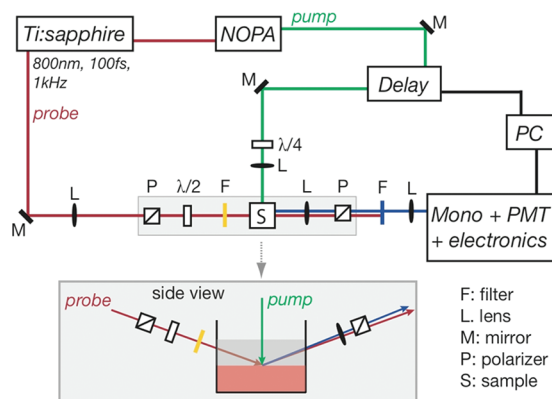

Figure 5. Schematic layout of a typical TR-SSHG setup.

described here in some detail to illustrate the current possibilities and limitations. This setup is based on a Ti:Sapphire-amplified system producing ∼100 fs pulses at 800 nm and 1 kHz. Part of the output feeds a noncollinear parametric amplifier to generate pulses tunable between ∼480 and ∼700 nm used for pumping. A wave plate serves to adjust the polarization before the pump beam is focused on the sample. Another fraction of the 800 nm amplifier output is directly used for probing, and its polarization is controlled via a half-wave plate. A filter in front of the sample eliminates spurious second-harmonic light that could be generated at metallic mirrors before the probe pulses reach the sample, and another filter after the sample suppresses the reflected probe pulses from the second-harmonic signal generated at the interface. This signal then passes a polarizer and a monochromator before it eventually reaches the photodetector and is processed with a computer-controlled gated boxcar averaging device. Typical energies at the sample are of the order of 1−2 μJ for the pump and <1 μJ for the probe beam with spot sizes of around 1 mm in order not to saturate the probed resonance.

> The experimental tools used up to now are still relatively primitive compared to the level of sophistication of the spectroscopic techniques applied for studying photoinduced processes in bulk solution.

Other setups additionally allow tuning the probe wavelength, giving more flexibility in the choice of molecules. Nevertheless, probing is in most cases only done at a single observation wavelength, making the interpretation of the experimental data very difficult, especially when working in a time scale where processes like solvent and vibrational relaxation lead to spectral dynamics. In any case, the bulk behavior of the molecule has to be precisely known in order to be able to draw any conclusion from such data.

Because the interfacial response of the molecules is often weak, TR-SSHG and TR-SSFG signals are generally noisy,

limiting the accuracy of the measured time constants and the possibilities of data interpretation, especially if the observed differences are small. Averaging over a long acquisition time is only a partial solution as prolonged excitation of the sample can lead to photodegradation. Unfortunately, a liquid/liquid interface cannot be refreshed as easily as a bulk solution.

Some of the current experimental limitations can be overcome by performing broad-band detection. This approach has been recently demonstrated with electronic TR-SSFG.[18,19] Probing was achieved by SSFG of a 800 nm pulse with a white light pulse generated by self-phase modulation in water, and the resulting signal was then dispersed in a spectrograph and detected by a CCD camera. The quality and information content of the data obtained with rhodamine 800 and MG at the air/water interface was comparable to bulk transient absorption measurements to an extent that even a global analysis of the data became feasible.[18,19]

In all of the above-mentioned examples, homodyne detection of the SSHG or SSFG signal was performed, the signal intensity being proportional to $|\chi^{(2)}|^2$. The response from molecules probed resonantly has both real and imaginary parts, whereas the response from the solvents, which is nonresonant, is only real. If this nonresonant response is negligibly small, the change of signal intensity in a time-resolved experiment is directly proportional to the square of the population change. This is, however, no longer the case if the nonresonant contribution differs from zero as it interferes with the real part of the resonant response and distorts the time profile of the signal intensity. One solution to this is heterodyne detection, where the SSHG or SSFG signal is mixed with an optical field of the same frequency and in-phase with the field generated from the imaginary part of the susceptibility. The advantages are an amplification of the resonant signal and a linear relationship between signal intensity and population changes. This detection has already been demonstrated for stationary vibrational and electronic SSFG but not for TR-SSFG.[41,42]

A further development of these techniques could be 2D-SSHG, analogous to the setup recently reported for vibrational SSFG.[17] This would be an extremely powerful method for investigating solvation dynamics and the interaction between probe molecules at interfaces.

In addition to these spectroscopic developments, further effort should also be made on the theoretical side. Until now, the data interpretation has been mostly performed on a qualitative basis in the limit of a two-level system. At the moment, our understanding of the exact relationship between a transient absorption spectrum measured in a bulk experiment and the expected TR-SSHG or TR-SSFG spectra is very limited. Such knowledge is needed to avoid misinterpretation. The recent theoretical treatment of orientational diffusion at the interface performed by Fayer and co-workers clearly demonstrates the pitfall of too simplistic a data analysis.[29] Molecular dynamics simulations represent also a powerful additional tool to improve our understanding of liquid interfaces and to help the interpretation of experimental data. Some effort, which gave new insight into the structure and dynamics of interfaces, has already been done.[43−46] However, less information is available so far about the dynamic properties of solute molecules adsorbed at a liquid interface.

Theoretical development requires reliable experimental data, and clearly important concerted efforts in all of these directions are still required before our knowledge on the dynamics of photoinduced processes at liquid interfaces can reach a level

similar to the one that can nowadays be attained in bulk solution.

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Ultrafast spectroscopy at liquid interfaces is still an almost unexplored area that probably conceals many traps but most certainly holds several beautiful treasures.

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Notes
The authors declare no competing financial interest.

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