Study of water using ultrafast lasers

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Some of the peculiar phenomena occurring in the aqueous solutions have been studied using an ultrafast laser. It is observed that the dynamics of the intramolecular charge transfer process is markedly retarded when the probe solute is transferred from bulk water to the interior of various hydrophobic aggregates. Solvation dynamics of water molecules in various organized and biological environments is found to be more than thousand times slower than that in ordinary water. Lastly, several processes occurring at the water surface have been studied using the novel surface second harmonic generation technique.

The recent progress in ultrafast laser spectroscopy has vastly improved our understanding of the dynamics of many processes occurring in liquids. The unprecedented time resolution down to femtosecond (10^{-15} s) timescale has revealed detailed information on the early events of many ultrafast processes. Among all liquids, simple aqueous solutions are of special interest because of their inherent complexity and the fundamental role played by water in many chemical and biological processes. The uniqueness of water is manifested in a large number of phenomena which occur exclusively in the aqueous medium. For instance, many organic molecules exhibit a marked tendency to form aggregates in aqueous solutions so as to minimize water–organic interfacial area. This tendency, known as the hydrophobic effect, arises from the difference in the very strong water–water interaction and the relatively weak water–organic interactions. The hydrophobic effect is responsible for a large number of binding processes occurring in water such as the enzyme–substrate binding, antigen–antibody binding, formation of micelles and other supramolecular assemblies and also for the compact binding of reactants which causes acceleration of bimolecular organic reactions in water. There is considerable recent interest in chemistry in such supramolecular assemblies. The local environment around a fluorophore in such a hydrophobic aggregate is considerably less polar than bulk water. As a result, dynamics of many processes, which depends on the local polarity, is affected significantly when the probe solute is transferred from the bulk water to the interior of these aggregates. The twisted intramolecular charge transfer (TICT) process is one such process. In the first part of this account we will discuss how the hydrophobic binding affects the intramolecular charge transfer processes of some organic fluorophores.

Secondly, one of the longstanding goals of chemistry and biology has been to unravel the dynamics of the water molecules bound to proteins and other organized assemblies. We will discuss results of some recent experiments which demonstrate that the relaxation dynamics of the water molecules in many organized assemblies is several thousand times slower compared to the ordinary water molecules.

Thirdly, due to the very high surface tension of water, many organic molecules easily get adsorbed at the water surface. This plays an important role in marine life and pollution of sea and rivers. We will describe some applications of a novel technique, surface second harmonic generation, to study the air–water interface. This new technique is based on a nonlinear optical effect and requires very high peak power of the exciting laser light. Since the peak power of a laser is equal to the pulse energy divided by the pulse duration, even with a pulse feeble in energy (e.g. nanojoules), one can get megawatt power if the pulse duration is one femtosecond. The tremendous intensity of the ultrafast lasers allows observation of many nonlinear optical processes even when the sample concentration is rather low.

TICT processes in hydrophobic aggregates

The TICT process is exhibited by molecules in which an electron donor and an acceptor is connected by a flexible bond. On electronic excitation such molecules initially form a 'nonpolar' state. Subsequently, an electron is transferred from the donor to the acceptor and this is accompanied by a twist about the flexible bond joining the donor and the acceptor (Figure 1). The resulting highly polar state is known as the TICT state. Since during the TICT process the molecule goes from a 'nonpolar' state to a highly polar state, the transition state is more polar than the reactant. Consequently, the activation energy for the TICT process decreases with rise in the polarity of the medium. For many molecules (e.g. dimethylnitrobenzene (DMABN) etc.) emission

Figure 1. Twisted intramolecular charge transfer process.
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occurs from both the nonpolar and the TICT state. However, for many other molecules (e.g., nile red, anilino-naphthalene sulphonates and coumarin laser dyes) the TICT state is nonemissive. For these molecules, the TICT process is just a nonradiative, dissipative process occurring in the nonpolar excited state as a result of which the lifetime and intensity of the emission from the nonpolar state decrease. Due to the polarity dependence of the rate of the TICT process, the lifetime and emission quantum yield of the nonpolar emission is extremely sensitive to the medium. For instance, in the case of 2-p-toluidino-6-naphthalene sulphonate (TNS), while the lifetime and emission quantum yield in dioxane are 8 ns and 0.32 respectively, in water its lifetime decreases over hundred times to 0.06 ns and the quantum yield to 0.001. Due to this remarkable polarity sensitivity, TNS is widely used as a biological probe. The TICT process of DMABN, TNS, coumarin dyes and many other molecules has recently been studied in a wide variety of organized assemblies. The structures of some of these organized assemblies are given in Figure 1. The TICT process which occurs so fast (60 ps for TNS) in bulk water is observed to slow down appreciably when the probe (TNS, DMABN, etc.) is transferred from the highly polar bulk water to the relatively less polar interior of the organized assemblies. Table 1 summarizes the rate of the TICT process of TNS in a number of organized media. It should be noted that the mobile probe spans a region of space within its lifetime in the excited state. Based on the diffusion coefficients (D = 0.05 Å² ps⁻¹) of ordinary organic molecules in water and noting that the mean square displacement along a particular direction, \( \langle x^2 \rangle = 2D \langle \tau \rangle \), one expects the probe molecule to move about 1 nm per nanosecond and thus a probe having subnanosecond lifetime scans a region of radius less than 1 nm (ref. 35). Since lifetime of TNS in many organized medium is 2–3 ns, TNS faithfully reports the microscopic polarity of a region of dimension a few nm.

The hydrophobic binding of the TICT probe molecules to cyclodextrins and other polysaccharides is particularly important for their implications in the molecular recognition of cell surface polysaccharides and the drug delivery systems. Sugar molecules are generally considered to be highly polar due to their high solubility in water and preponderance of hydroxyl groups. However, the structural and stereochemical factors in many cases render one surface of a polysaccharide molecule only devoid of the hydroxyl groups and consequently, hydrophobic. Many organic molecules easily bind to such hydrophobic surfaces of a sugar and experience a polarity lower than that of water. For example, the cyclic polysaccharides, cyclodextrins (CDx) consist of a highly nonpolar and hydrophobic cavity with all the hydroxyl groups projected outward. The height of the CDx cavity is about 8 Å while the diameter of the cavity is 5, 6 and 8 Å for \( \alpha, \beta \) and \( \gamma \)-CDx which contains respectively 6, 7 and 8 \( \alpha \)-amylase units. The binding constants of many probes with \( \beta \)-CDx are usually higher than those with \( \alpha \)-CDx and often complexes with more than one stoichiometry are observed. The TICT process of TNS has been found to be 40–60 times retarded inside the CDx cavity, causing enhancement of the intensity and lifetime of the nonpolar emission. Cyclodextrins of different sizes are observed to affect the TICT process differently. For example, while \( \alpha \)-CDx causes an enhancement of the TICT emission of DMABN causing little or no change of the nonpolar band, \( \beta \)-CDx causes enhancement of both the nonpolar and the TICT emission. This is attributed to the formation of different kinds of complexes for different CDx. Very recently Al-Hassan et al. reported that while fresh aqueous DMABN solution containing \( \alpha \)-CDx shows no enhancement of the nonpolar emission, large enhancement of the nonpolar emission is observed when the solution is kept for three months. DMABN often contains an impurity which absorbs at wavelengths longer than 340 nm and gives rise to an emission around the same region as the nonpolar emission band of highly purified samples of DMABN. Al-Hassan et al. did not report the absorption spectra of their old solutions but their excitation spectra exhibit significant intensities above 340 nm. Thus the effect reported by Al-Hassan et al. may be due to some impurities produced by decomposition of DMABN in the old solutions.

The linear polysaccharide dextrin has been reported to display hydrophobicity in their ability to solubilize lipophiles and modulate rates of chemical reaction. Dextrin causes nearly 50 times enhancement in the

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Figure 2. Structure of different organized assemblies: (a) cyclodextrin, (b) micelles, and (c) reverse micelles.

Table 1. Emission properties of TNS in different environments

<table>
<thead>
<tr>
<th>Medium</th>
<th>( \Phi_i )</th>
<th>( \tau_i ) (ns)</th>
<th>( k_{\text{exc}} ) (× 10⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.001</td>
<td>0.06</td>
<td>16.6</td>
</tr>
<tr>
<td>( \alpha )-CDx</td>
<td>0.046</td>
<td>1.69</td>
<td>0.56</td>
</tr>
<tr>
<td>( \beta )-CDx</td>
<td>0.064</td>
<td>2.43</td>
<td>0.39</td>
</tr>
<tr>
<td>Dextrin</td>
<td>0.060</td>
<td>2.86</td>
<td>0.33</td>
</tr>
<tr>
<td>Dextran</td>
<td>0.004</td>
<td>0.51</td>
<td>1.95</td>
</tr>
</tbody>
</table>

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intensity and lifetime of the nonpolar emission of TNS presumably due to hydrophobic binding of TNS to dextrin\(^{23}\). In contrast, another linear polysaccharide, dextran, causes very slight enhancement of TNS emission, suggesting that for dextran both the surfaces are quite hydrophilic. Energy minimization calculation also indicates that while dextrin has a hydrophobic surface, dextran has none\(^{23}\).

Different additives affect the hydrophobic aggregation\(^{1-3}\). Urea and big ions usually enhance water–organic interactions and hence are called salting-in agents. The salting-in agents increase solubility of organic molecules in water, cause denaturation of proteins, inhibit formation of micelles, retard bimolecular reactions in water and in general break hydrophobic aggregates. On the other hand, small ions, known as the salting-out agents, usually reduce solubility of organic molecules in water, accelerate bimolecular reactions and enhance hydrophobic binding. In recent years there have been many attempts to elucidate the mechanism of action of such agents\(^{3,7,38}\). The so-called indirect mechanism envisages that urea completely disrupts the hydrogen-bonded structure of water and thus affects the solvation of organic and biomolecules in water. According to the direct mechanism, however, urea does not disturb the water structure but displaces several water molecules from the immediate neighbourhood of an organic molecule in water and thus modifies water–organic interaction by acting as a bridge between them. The recent computer simulations\(^{97,38}\) and experimental results\(^{1}\) go against the indirect mechanism and support the direct mechanism. The effect of different salting-in and salting-out agents on the hydrophobic binding of TNS with cycloextrin and dextrin has been studied in detail\(^{16-18}\). Binding studies indicate that urea, Cs\(^+\), guanidinium and perchlorate ions cause a decrease in the fraction of TNS molecules bound to CDx or dextrin. Thus urea and salting-in agents directly interact with the fluorophores bound to the organized assemblies and actually ‘unbind’ them. This lends strong support to the direct mechanism. As a result, addition of salting-in agents causes reduction in the fluorescence intensity and increase in the amplitude of the component of the fast decay corresponding to free TNS in bulk water. Small ions (Li\(^+\), Cl\(^-\) etc.), on the contrary, increase the fraction of bound TNS molecules. Tetra-n-butyl ammonium (TBA) ion being a big one is expected to break hydrophobic aggregates of TNS and CDx, causing decrease in the emission intensity. However, with TBA large fluorescence enhancement of TNS, over and above that caused by CDx, is observed. To explain this, it is proposed that since TBA cations itself form micellar aggregates they form ternary aggregates containing CDx, TNS anion and TBA cation\(^{21}\). In such a complex the local polarity around TNS decreases further as the four butyl groups wrap around the TNS:CDx complex.

Solvation dynamics of water molecules in organized assemblies

The solvation process refers to the reorganization of polar solvent molecules around a dipole created instantaneously in a liquid by a picosecond or femtosecond pulse. The recent activity in this area has generated a wealth of information on the solvation dynamics in many homogeneous solutions\(^{39-57}\). The most popular technique for studying solvation dynamics is the method of time dependent Stokes’ shift (TDSS). It is based on the fact that as solvation proceeds the energy of the probe solute decreases and thus with time its emission spectrum moves to lower energy, i.e. towards red. Thus, if \(\nu(0)\), \(\nu(t)\) and \(\nu(\infty)\) denote emission frequencies at time zero, \(t\) and infinity, \(\nu(0) > \nu(t) > \nu(\infty)\). The solvent correlation function \(C(t)\) is defined by

\[
C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}.
\]

The time constant of decay of \(C(t)\) is known as the solvation time. In many cases the decay of \(C(t)\) is multieponential (e.g. \(\Sigma(a_\nu \exp(-t/\tau_\nu))\)). In such a case one often uses the average solvation time \(\Sigma(a_\nu \tau_\nu)\). According to the continuum theory, the time constant of decay of \(C(t)\) is the longitudinal relaxation time \(\tau_L = (\varepsilon_\infty - \varepsilon_s)\tau_D\), where \(\varepsilon_s\) and \(\varepsilon_\infty\) are respectively the static and high frequency dielectric constants of water and \(\tau_D\), the Debye relaxation time. Since for water \(\varepsilon_s = 78\) and \(\varepsilon_\infty = 5\) and \(\tau_D = 8\) ps one immediately expects a solvation time of about 500 fs for water. The actual experimental result indicates presence of a major component of 310 fs (refs 44, 45). Recently Nandi et al.\(^{48}\) and Schwartz and Rossky\(^{46}\) analysed the experimental results on the solvation dynamics in water in considerable detail taking into account effect of the different vibrational modes of water and isotopic substitution by deuterium.

More recently, several groups initiated studies on the relaxation dynamics of water in many organized environments with a view to understanding the behaviour of the water molecules bound to proteins and other organized assemblies and perturbed by the local electrostatic attractions and hydrogen bonds\(^{45}\). The dielectric relaxation and pulsed NMR studies of biological systems indicate that while ordinary water exhibits a single fast relaxation time of 8 ps, in biological systems one often observes a bimodal decay with one component around 10 ps and another very long component in the 10 ns time scale\(^{45,58-61}\). The exact origin of the almost universally observed bimodal dielectric decay of biological systems is not yet completely understood. The earlier workers relied on a simplified model involving two
kinds of water, 'free' and 'bound' with relaxation times of 10 ps and 10 ns respectively. However, Nandi and Bagchi have proposed a model which envisages an equilibrium between the bound and the free water where the nanosecond component arises not because of the slowness of the bound water but because of the need for the establishment of equilibrium.

Fleming et al. first applied the TDSS technique to study the solvation dynamics in a CDx cavity. They observed that while in pure water the solvation dynamics occurs in the subpicosecond time scale, in the γ-CDx cavity the solvation dynamics occurs in the nanosecond times scale. Nandi and Bagchi ascribed the nearly thousand-fold retardation of the solvation dynamics inside the γ-CDx cavity to the freezing of the translational degrees of freedom of the water molecules inside the γ-CDx cavity.

Sarkar et al. extended this study to investigate the solvation dynamics of water molecules in reverse micelles and micelles using the TDSS technique while Bright et al. used phase fluorimetry to study solvation dynamics in reverse micelles. The reverse micelles are basically a nanometer-sized water droplet (water pool) surrounded by a layer of surfactant molecule and dispersed in a hydrocarbon solvent. The radius (r_w) of the water pool may be varied from a few Å to 100 Å by varying the ratio of the water molecules and the surfactant molecules. Obviously in a small water molecule, the water molecules are very rigidly held by the ionic headgroups of the surfactants and the counterions and hence are very slow. In a big water pool, though the water molecules at the peripheries are rather strongly held, those at the centre are relatively free. Thus for reverse micelles while the solvation dynamics in a small water pool of radius < 10 Å occurs with a time constant 8 ns, in big water pools (r_w > 20 Å) a much faster component of about 2 ns appears. The observation of the nanosecond component may be semiquantitatively explained as follows. The static dielectric constant of the water pool can be estimated from the position of the emission maxima of various polarity-sensitive probes. The result indicates that the dielectric constant of the water pool is close to that of alcohol, i.e., ~30. If one assumes that the high frequency dielectric constant of water in the reverse micelle is the same as that of water, i.e., 5 and the τ_s = 10 ns one readily gets a solvation time of 1.67 ns.

Das et al. have studied the deuterium isotope effect of 4-aminophthalimide on the solvation dynamics in reverse micelle. They reported a 20% reduction in the average solvation time in D_2O compared to water. This is consistent with the 25% slower dielectric relaxation time of D_2O compared to H_2O (ref. 61) and shows that D_2O is slower than H_2O. Similar isotope effect on the solvation dynamics and electron solvation has been reported in homogeneous liquids and micelles. It appears that the deuterium isotope effect is most prominent when the probe interacts strongly with the surrounding water molecules.

Recent small angle neutron scattering studies indicate that in aqueous solutions micelles consist of a 'dry' hydrocarbon core surrounded by 'wet' spherical shell of thickness 6-7 Å (ref. 66, 67). This shell, called the Stern layer, contains the polar head groups of the micelles, counterions and considerable amount of water. Sarkar et al. studied solvation dynamics of coumarin 480 in the Stern layer of neutral (triton X), cationic (cetyltrimethyl ammonium bromide, CTAB) and anionic (SDS) micelles. They observed that the water molecules present in the Stern layer of the micelles though much slower than the ordinary water molecules, are faster than those in the CDx cavity or those in the reverse micelles. Table 2 summarizes solvation times of water in different organized environments.

### Surface second harmonic generation

Second harmonic generation or, more generally, sum frequency generation is a nonlinear optical process in which two laser photons of frequency ν_1 and ν_2 interact with a medium to produce a nonlinear polarization, P(2ω) which gives rise to a radiation at a frequency ν_1 + ν_2. Second harmonic generation (SHG) is the special case of sum frequency generation where ν_1 = ν_2 = ν. In the case of SHG, P(2ω) is given by, P(2ω) = χ(2) EE, where χ(2) is second order nonlinear polarization of the medium. Due to symmetry reasons χ(2) vanishes in a centro-symmetric medium. Thus second harmonic generation does not occur in any centrosymmetric medium. The bulk of any liquid is centrosymmetric due to isotropic arrangement of the molecules and hence does not give rise to SHG. However, the symmetry is broken at the surface or in general at the interface of any two bulk media. Thus SHG or SFG can selectively probe any interfaces. Since no other optical technique possesses such surface selectivity, surface SHG (SSHG) and surface SFG (SSFG) have become two very powerful and popular techniques to study various interfaces. In the present article we will restrict ourselves to only air–water interface.

In the absence of any local field χ(2) is given by,

<table>
<thead>
<tr>
<th>Medium</th>
<th>Average solvation time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>&lt;0.31</td>
</tr>
<tr>
<td>AOT reverse micelle, r_w &lt; 10 Å</td>
<td>8000</td>
</tr>
<tr>
<td>AOT reverse micelle, r_w &gt; 20 Å</td>
<td>2000</td>
</tr>
<tr>
<td>CTAB</td>
<td>474</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>1176</td>
</tr>
<tr>
<td>SDS</td>
<td>693</td>
</tr>
</tbody>
</table>
\( \chi^{(2)} = N_i \langle \alpha^{(2)} \rangle \), where \( N_i \) denotes the number of molecules at the surface, and \( \alpha^{(2)} \) is the second order polarizability with the angular bracket denoting orientational average. \( \chi^{(2)} \) and \( \alpha^{(2)} \) both contain 27 elements. However, using the symmetry property of the surface one can show that many elements of \( \chi^{(2)} \) vanish and many become equal to one another and thus the \( \chi^{(2)} \) for surface species is described by only three independent components. For many molecules \( \alpha^{(2)} \) is dominated by a single component and this is known as the uniaxial case. A typical SSHG setup is shown in Figure 3. In a SSHG experiment one measures three properties of the SSH light – intensity, polarization and phase, which are respectively related to the number, average orientation and absolute orientation of the surface species. The square root of the intensity of the SSH light is proportional to \( N_i \) and can be used to test different adsorption isomers. For many organic compounds adsorption at the water surface obeys the Langmuir adsorption isotherm. From this the free energy of adsorption of a series of \( \rho \)-alkyl substituted phenols and anilines and their corresponding anions and cations have been determined. It is observed that for any phenols (or anilines) the free energy of adsorption of the neutral species is more negative than that of the charged phenolate (or anilinium) ion. This is because the charged species are solvated to a lesser extent at the surface than they are in the bulk water. Because of this for smaller phenolates the population of the ions at the surface is negligibly small. Thus the simple dissociation equilibrium of phenol remains largely in favour of the neutral species. In other words, the pKa at the water surface is different from that in the bulk. However, as the size of the alkyl group at the para position increases, the surface populations of the charged phenolates increase due to the hydrophobic effect.

It is evident that the enrichment of the water surface by organic molecules arises because of the hydrophobic effect and an organic molecule is stabler at the water surface than it is in the bulk because when the molecule is at the water surface it disrupts fewer number of water–water bonds. Since as noted earlier urea and other salts affect water–organic interaction they are expected to affect surface population of the organic molecules. To investigate this phenomenon one needs to monitor only one surface species in the presence of others. This is possible using the resonance SSHG technique. The quantum mechanical expression of \( \chi^{(2)} \) contains energy denominators of the form \( (\Delta E - \hbar \nu) \) and \( (\Delta E - 2\hbar \nu) \). Obviously, \( \chi^{(2)} \) becomes very high when the energy gap \( \Delta E \) becomes equal to \( \hbar \nu \) (one-photon resonance) or \( 2\hbar \nu \) (two-photon resonance). In the case of resonance SSHG the signal of the resonant species is so much higher than that of the non-resonant species (water or a surfactant, CTAB) that the latter may be considered silent. Thus using resonance surface second harmonic generation one can selectively monitor one surface species in the presence of others. \( \rho \)-Nitrophenol (PNP), which absorbs around 300 nm, is two-photon resonant for a fundamental laser wavelength of 600 nm. As a result, signal from PNP is 100 and 50 times larger than that of pure water and CTAB surfaces. Sarkar et al. studied the effect of CTAB, urea and different salts on PNP at the water surface. It is observed that for all those additives while the intensity of the SSH signal changes substantially the orientation of the molecule at the surface remains the same. Thus the intensity change is not due to any change in the orientation of the PNP molecules at the water surface and is related to change in the surface population of PNP. On addition of urea and salts containing big ions (perchlorate and guanidinium) the intensity of the SSH signal decreases sharply while the salts containing small ions (LiCl) cause an appreciable increase in the intensity of the SSH signal. It is observed that the free energy of adsorption changes on addition of urea and these salts and the variation in surface population and hence the intensity of the signal can be described in terms of the change in free energy. CTAB causes a ten-fold increase in the intensity of the SSH signal of PNP at a concentration nearly one-fourth of the reported critical micellar concentration and above this the intensity of the signal remains more or less the same. This indicates that the surface structure changes considerably much before the micellar aggregates are formed at the bulk. In the case of CTAB both orientation and free energy of adsorption remains the same. This indicates that CTAB increases the surface population of PNP by increasing maximum capacity of the surface to accommodate PNP. This is similar to the enrichment of the biomembranes by organic molecules. Since PNP is more soluble in hydrocarbon.

![Figure 3. Schematic of a surface second harmonic generation setup.](image)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Intensity (counts/( \mu ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>5 M urea</td>
<td>7</td>
</tr>
<tr>
<td>0.2 mM CTAB</td>
<td>600</td>
</tr>
<tr>
<td>0.2 mM CTAB + 7 M urea</td>
<td>63</td>
</tr>
<tr>
<td>5 M LiCl</td>
<td>110</td>
</tr>
<tr>
<td>5 M LiClO₄</td>
<td>15</td>
</tr>
<tr>
<td>5 M guanidinium chloride</td>
<td>15</td>
</tr>
</tbody>
</table>

*Table 3. Effect of additives on SSHG signal of PNP at the water surface*
than in water it enriches the water surface more when it is covered by alkyl chains of the surfactant than it does for the pure water surface. Table 3 summarizes the relative signal intensities of PNP at the water surface. It is observed that for insoluble monolayers at the water surface the surface population of PNP increases until the surface area per molecule decreases to a particular value\textsuperscript{20}. On further increase in the surface pressure the surfactant pushes the PNP molecules away from the surface and the signal drops sharply. Recently, Eisenenthal et al.\textsuperscript{24} determined the polarity of the water surface using spectroscopy of \(p-N,N\)-dimethylamino nitrobenzene whose absorption energy is polarity-dependent. The results indicate that the polarity of water surface is similar to that of butyl ether or \(CCl_4\).

Another important issue is how the water surface affects the dynamics of the ultrafast processes. Using time-dependent resonance SSHG, Eisenenthal\textsuperscript{8} demonstrated that the rate of the photoisomerization of DOCCI and malachite green is different at the water surface than that in the bulk water. For DOCCI, a rod-shaped cationic dye, the rate at the water surface has been found to be three times faster than that in the bulk while for malachite green, a nearly planar molecule, the isomerization process is three times slower at the surface. Thus compared to bulk water DOCCI experiences a lower friction at the surface while malachite green experiences a higher friction. To explain the difference in the friction reported by the different probes it is proposed that DOCCI and malachite green probe different parts of the interface.

Conclusion and future outlook

The behaviour of the water molecules continues to intrigue and fascinate scientists of diverse disciplines. It is quite natural to expect that with the development of newer arsenals, both in the theoretical and the experimental front, many new aspects of water would be attacked which has been hitherto impossible or difficult to tackle. The ultimate goal of elucidating the structure and dynamics of water in the liquid state and in all kinds of organized assemblies taking into account all the microscopic interactions still remains a formidable task. But the new results outlined in this account have certainly generated considerable enthusiasm and provided new insight on how water controls the structure, dynamics and reactivity of organic and biomolecules both in the bulk and at the surface. The most satisfying outcome of any study on water is that it brings us closer to nature and life.


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