

# Rotational Relaxation at the Air/Water Interface by Time-Resolved Second Harmonic Generation

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Time-resolved surface second harmonic generation has been used to study the picosecond rotational relaxation dynamics of free Rhodamine 6G molecules at the air/water interface. It was found that different elements of the second-order nonlinear susceptibility,  $\chi^{(2)}_{ijk}$ , show different kinetics, which indicates that rotational motions have been observed. The data also suggest that the observed rotational relaxation is due chiefly to the out-of-plane motions at the interface and that the ground- and excited-state molecules have different equilibrium orientational distributions.

Molecular motion in liquids has been an active area of experimental and theoretical research for many years and continues to play an important role in studies of molecular forces in liquids as well as in restricted environments of membranes, micelles, and vesicles.<sup>1-6</sup> Continuing along the line of these efforts, we have undertaken the study of rotational motions at the air/water interface. Unlike the bulk liquid, molecules at a surface experience an asymmetric environment due to different bulk media on either side of the interface. It is therefore of fundamental interest to study the molecular dynamics in this unique environment.

In this Letter, we present our preliminary results on the first direct observation of the orientational relaxation of Rhodamine 6G molecules at the air/water interface by surface second harmonic generation (SHG).<sup>7-17</sup> The key feature of SHG that makes this experiment feasible is that SHG is electric dipole forbidden in the bulk but allowed at the interface where the symmetry is broken. Information about the relative populations and orientations of adsorbates at the air/water interface can be readily obtained, because the observed reflected SH field amplitude,  $E_{2\omega}$ , is proportional to the surface nonlinear susceptibility,  $\chi^{(2)}$ , which, neglecting local field effects, is the product of the population per unit area of adsorbates,  $N$ , and the orientational average of the nonlinear polarizability,  $\langle \alpha^{(2)} \rangle$ .

There have been studies on orientational relaxation of molecules at interfaces using other techniques, e.g., fluorescence depolarization.<sup>18</sup> However, in those cases, the molecules studied were attached to a long hydrophobic chain in order to make them insoluble in the bulk liquid. This avoids any fluorescence contribution from the much larger bulk population that would result, and which would consequently overwhelm any interfacial fluorescence. As a result of the attached hydrophobic chain, the motions of the molecules were hindered at the interface. By taking advantage of the fact that SHG is surface specific, we can directly study free molecules at an interface even when there is a large population in the bulk liquid.

The idea of the experiment is to use a polarized 355-nm picosecond laser pulse, traveling perpendicular to the surface of a 20  $\mu$ M Rhodamine 6G aqueous solution, to disturb the equilibrium orientational distribution at the interface, by preferentially exciting those molecules whose transition moments have a large component along the polarized light field. The relaxation of the perturbed distribution is monitored by observing the SH signal generated by a time-delayed second polarized pulse at 532 nm (Figure 1). The SH signal changes markedly upon photoexcitation, since the nonlinear polarizability of the excited molecules is different from that of the ground-state molecules. The SH signal continues to change with time as the excited- and ground-state molecules undergo rotational motions toward their respective equilibrium orientational distributions and as the excited molecules relax back to the ground state. To minimize the effects of energy transfer and dimerization on the observed kinetics the interface population was kept low ( $4 \times 10^{12}$  molecules/cm<sup>2</sup>). At these low concen-

trations we found that the dynamics did not change when the interface population was doubled. We therefore conclude that intermolecular energy transfer and dimerization, both concentration-dependent processes, were not affecting the orientational relaxation kinetics that we were measuring.

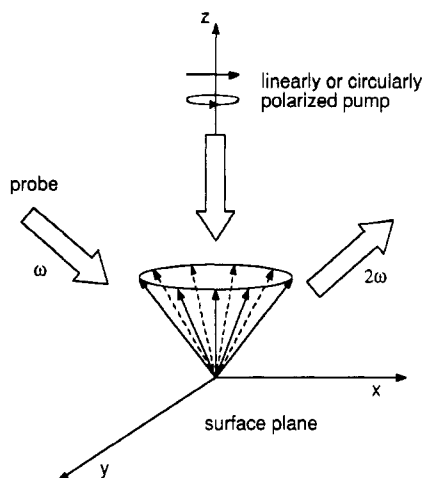
We obtained the time dependence of two different elements of the second-order nonlinear susceptibility, namely  $\chi^{(2)}_{zzx}$  and  $\chi^{(2)}_{xxx}$ , which can be expressed as

$$\chi^{(2)}_{ijk} = N \sum \langle T_{ijk}^{lmn} \rangle \alpha^{(2)}_{lmn}$$

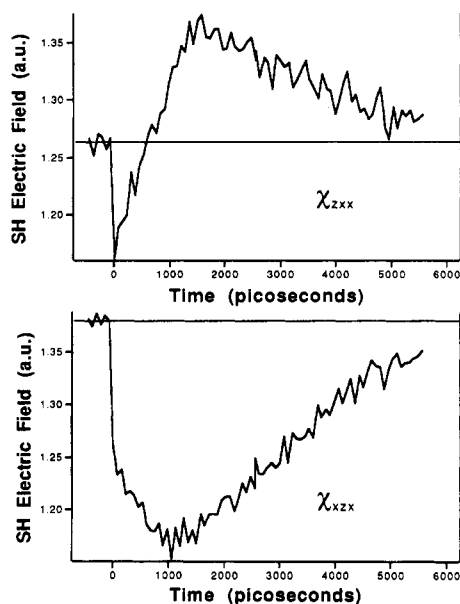
where  $\langle T_{ijk}^{lmn} \rangle$  is the direction cosine matrix that transforms the laboratory axis ( $i, j, k$ ) into the molecular axis ( $l, m, n$ ). The time evolution of the SH signal is due to the change in the relative population of ground- and excited-state molecules, and due to orientational changes in the ground- and excited-state distributions. Figure 2 shows the time dependence of  $\chi^{(2)}_{zzx}$  and  $\chi^{(2)}_{xxx}$ . At negative times, before the pump pulse has arrived, only ground-state molecules are being probed. Right after photoexcitation we observed in both cases a sharp, instrument-limited decrease in signal, due to the decrease in the total nonlinear susceptibility  $\chi^{(2)}$ . This decrease can be due to the excited-state nonlinear polarizability,  $\alpha^{(2)*}$ , being smaller than the ground-state nonlinear polarizability,  $\alpha^{(2)}$ , due to resonance effects. After this initial decrease in signal,  $\chi^{(2)}_{zzx}$  increases, and in about 600 ps it increases beyond the value corresponding to negative time, reaching a maximum value in about 1.5 ns. The signal then returns back to the original

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**Figure 1.** Schematic experimental setup. The arrows represent the molecular transition dipoles arranged to a common origin. The linearly or circularly polarized pump disturbs the equilibrium orientational distribution at the interface. The relaxation of the perturbed distribution is monitored by observing the SH signal ( $2\omega$ ) generated by a time-delayed probe ( $\omega$ ).



**Figure 2.**  $\chi_{zxx}^{(2)}$  and  $\chi_{xzx}^{(2)}$  components of the second harmonic signal from the surface of a 20  $\mu\text{M}$  Rhodamine 6G aqueous solution versus probe delay time.

ground-state value in 5–6 ns. The observation that  $\chi_{zxx}^{(2)}$  first decreases and then exceeds the negative time value suggests the possibility that the equilibrium orientational distribution of the photoexcited molecules differs from that of the ground-state molecules and contributes more to the total  $\chi_{zxx}^{(2)}$  because of the more favorable orientation of the excited molecules. It would not be surprising if the change in the charge distribution of the solute molecules on photoexcitation produced a change in the equilibrium orientations of the excited molecules due to the change in solute–water interactions at the interface. However, for  $\chi_{xzx}^{(2)}$ , after the initial decrease there is a further decrease in signal that reaches a minimum in about 1 ns. Again, after 5–6 ns the signal approaches the initial ground-state value. Our data clearly show

a polarization dependence of the dynamics in that different elements of the SH signal show different time dependences. If there were no rotational motions involved, the time-dependent SH signal for  $\chi_{zxx}^{(2)}$  and  $\chi_{xzx}^{(2)}$  would be due to population relaxation only. The kinetics would then be the same for both elements, arising only from the excited-state population decay. However, this is clearly not the case. From the polarization-dependent kinetics we conclude that rotational motions are responsible for these observations.

In order to differentiate in-plane and out-of-plane molecular motions, we performed an experiment using circularly polarized light to excite the molecules isotropically in the surface plane. For the case of linearly polarized excitation, molecules are excited preferentially along a given axis in the interface and one would anticipate that the resulting anisotropy in orientations with respect to the in-plane axes would relax due to in-plane rotational motions of the molecules. One therefore might have expected the rotational kinetics observed to differ for the linearly and circularly polarized excitations. However we find that the dynamic curves for  $\chi_{zxx}^{(2)}$  and  $\chi_{xzx}^{(2)}$  for linearly and circularly polarized excitation are qualitatively the same, thus indicating that the observed rotational relaxation is due chiefly to the out-of-plane motions of the molecules at the surface. It must be emphasized that this result is not necessarily general and can be dependent on the relative pump/probe geometry as well as the susceptibility element measured, e.g., perhaps  $\chi_{zxx}^{(2)}$  having a different dependence on the orientational distribution would be more sensitive to the polarization of the pump light. In addition, the pump wavelength could affect this result since it determines the molecular axis of excitation and therefore the photogenerated orientational distribution at the interface.

In conclusion, rotational relaxation has been observed in the picosecond time scale at the air/water interface by time-resolved second harmonic generation. The rotational dynamics occurs within 1 ns, which appears to be slower than the 200-ps rotational relaxation time in bulk water.<sup>19</sup> A difference in either direction is not surprising since we are probing molecular motions at an interface where the potential field is asymmetric and likely to be quite different from that in the bulk liquid. From measurements of the strength of the SH signal we observed that one of the susceptibility elements,  $\chi_{zxx}^{(2)}$ , increased beyond its ground-state value on photoexcitation of interface molecules. We interpret this to be due to the different charge distribution in the excited-state molecules, which in turn yields an excited molecular orientational distribution which contributes more to the SH signal than that of the ground-state molecules. We also found that the longer time kinetics, interpreted as excited-state relaxation, appears to be comparable to that in the bulk aqueous solution (3.5 ns).<sup>20</sup> In addition, the data reveal that the rotational relaxation for the nonlinear susceptibility elements that we are measuring is due chiefly to the out-of-plane motions of the molecules at the surface. We are in the process of developing a model to quantitatively analyze our data and make comparisons with bulk liquid state results.

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