

Viscosity at Air/Water Interface revealed by Femtosecond TR-ESFG Spectroscopy

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Introduction

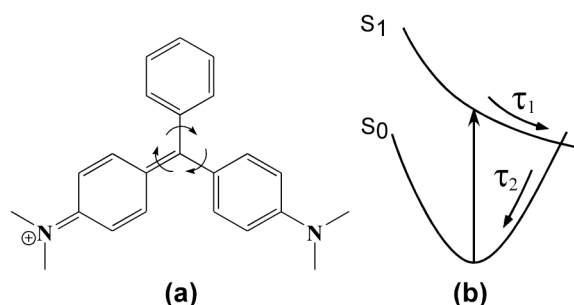
Triphenyl methane dyes, including malachite green (MG, Scheme 1a), have been extensively studied in the liquid phase because they can be the prototypes of barrierless chemical reactions in solution. The radiationless decay of the excited singlet state involves a rotation of the phenyl rings toward an equilibrium geometry displaced from that in the ground state (Scheme 1b).¹ The existence of an intermediate state (higher levels in S_0) in the ground state recovery (GSR) cycle will lead to a nonexponential GSR profile, as was observed by many researchers.¹ The GSR times of MG have been found to be proportional to the viscosity, η , of the medium.¹ The viscosity dependence of the excited state lifetime of MG, makes it a useful probe to monitor the viscosity of a medium.²

Even-order nonlinear spectroscopy is a very powerful and unique technique to study interfaces.³ We have recently developed the nonlinear multiplex time-resolved electronic sum frequency generation (TR-ESFG) technique (see figure 1) to measure interface specific transient electronic spectra of molecules.^{3b} In this study, we applied TR-ESFG spectroscopy to monitor the GSR dynamics of MG at the air/water interface and consequently, we determine the viscosity of the air/water interface. We also perform a temperature dependence study to clarify the effect of temperature on the air/water interface.

Results and Discussions

We performed a single colour pump-probe experiment to study bulk viscosity dependence of GSR dynamics of MG in different glycerol-water mixtures with varying viscosity. The measurements revealed two viscosity dependent time constants. From the fitting analysis, we found that the faster time constant follows a $\eta^{0.29}$ viscosity dependence while the slower component follows a $\eta^{0.45}$ viscosity dependence.

To measure the viscosity of the air/water interface we measured GSR dynamics of MG at the air/water interface by using our recently developed TR-ESFG technique. We observed two recovery time constants with a concentration dependent long-lived bleaching signal (Fig. 2). The existence of the two time constants in the GSR dynamics is consistent with the model of GSR dynamics in the bulk. Both the time constants are found to be slower compared to the bulk water. This indicates a hindered phenyl ring rotation of the MG molecule (consequently a higher viscosity) at the air/water interface. The temperature dependent studies at the air/water interface shows a strong temperature dependent behavior of the GSR dynamics. For example, at 2°C the two observed time constants are 4.6 ps and 31 ps while at 30°C they



Scheme 1. (a) Molecular structure of malachite green. (b) Schematic representation of excited state and ground state dynamics of malachite green.

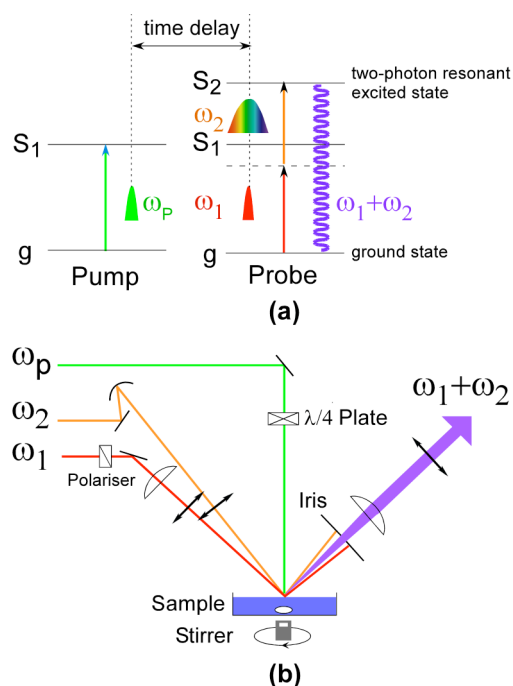


Fig. 1. (a) Experimental scheme of TR-ESFG spectroscopy. (b) Experimental setup of TR-ESFG spectroscopy.

decreased appreciably to 2.1 ps and 15.6 ps. This significant temperature dependence of GSR dynamics manifests the temperature dependent water structure at the air/water interface.

Comparing the results of the air/water interface with the viscosity dependent GSR dynamics of MG in the bulk solvent, we can readily see that the two observed time constants suggest two different viscosity values of the air/water interface (Fig. 3). In both cases the obtained viscosity is much higher than the viscosity of bulk water at a particular temperature. This dual nature of viscosity dependence of the two time constant may be the effect of the structure of the solvation shell around the molecule. In the ultrafast time regime, the phenyl rings first collide with a few solvent molecules in the first solvation shell. In later times, the collided solvent molecules are also faced collision with other solvent molecules in the outer shell and may show a higher viscosity.

The measured temperature dependent viscosity can be further exploited to determine the activation energy value for viscous flow at the air/water interface.⁴ The temperature dependence of the viscosity, η , is given by $\eta = A \exp(E_a/RT)$, where, A is a constant and E_a is the activation energy for viscous flow. E_a were determined by fitting a straight line to $\ln(\eta)$ versus $1/T$ (Fig. 4). In bulk water the activation energy for viscous flow is 17.9 kJ mol⁻¹. In contrast, at the air/water interface the activation energies are 63.4 and 33.4 kJ mol⁻¹ corresponding to the faster and slower GSR components respectively.

In conclusion, we determined the viscosity of the air/water interface by measuring the GSR dynamics of MG at the air/water interface using newly developed TR-ESFG spectroscopy. The observed GSR time constants are correlated with the viscosity of the air/water interface. It is readily seen that the viscosity at the air/water interface is much higher compared to the bulk water. From the temperature dependent study, the activation energy for viscous flow is found to be about 3.5 to 2 times higher at the air/water interface compared to the bulk water.

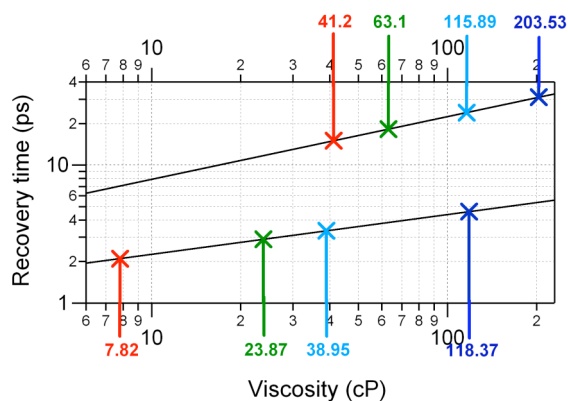


Fig. 3. Viscosity of the air/water interface directly obtained by comparing the GSR dynamics of MG at the air/water interface to the viscosity dependent GSR dynamics of MG in the bulk media at 4 different temperatures, viz. 30°C (red), 20°C (green), 10°C (cyan) and 2°C (blue).

References

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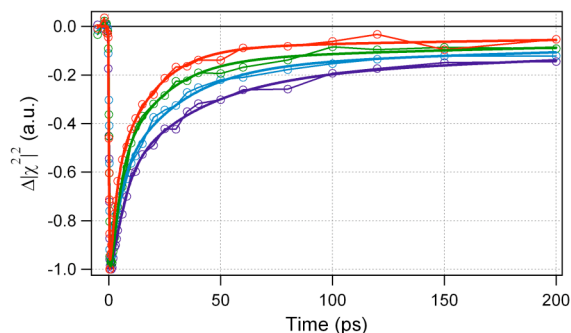


Fig. 2. Ground state recovery dynamics of MG at the air/water interface at four different temperatures, 30°C (red), 20°C (green), 10°C (cyan) and 2°C (blue). The bulk concentration of MG is 7 mM.

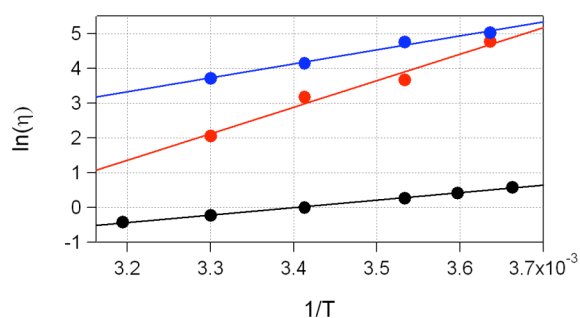


Fig. 4. Temperature dependent viscosity of bulk water (●) and air/water interface obtained from the faster (●) and from the slower (●) time constants. The solid lines correspond to the best fit Arrhenius type curves.