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## COMMUNICATIONS

## Dynamics of intermolecular electronic energy transfer at an air/liquid interface

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In this Communication, we wish to report preliminary results on picosecond time resolved studies of intermolecular electronic energy transfer between molecules at the air/liquid interface. We have used the technique of surface second harmonic generation (SHG)<sup>1-12</sup> to selectively probe the time dependent changes occurring in the interface<sup>13-15</sup> following photoexcitation of molecules by a pump pulse. The key feature of SHG that makes this experiment feasible is its sensitivity to the asymmetry of an interface located between centrosymmetric media. In the dipole approximation SH light is not generated in the bulk medium but is allowed at the interface. The SH light generated by the molecules composing the interface is dependent on the electronic states that they occupy. Prior to the excitation pulse the SH light generated by the probe pulse is due to ground state molecules. The photoexcitation by the pump pulse of some fraction of the interfacial solute molecules to their excited electronic states, changes their nonlinear polarizability  $\alpha^{(2)}$  and thus, the SH light generated. The SH light changes with time as the excited molecules decay back to their ground states. To better understand the energy transfer dynamics in the interface we measure the energy transfer dynamics<sup>16-19</sup> in the bulk region of the same solution by monitoring the fluorescence decay of the photoexcited donors using a picosecond streak camera.

The interfacial experiment consisted of exciting the donor rhodamine 6G ( $2 \times 10^{-4}$  M) to  $S_1$  with a 20 ps 532 nm pulse and monitoring the SH signal at 266 nm generated at the interface by a 532 nm probe pulse. We determined that no SH originating from the pump pulse reached the photodetector. The signal due to DODCI ( $2 \times 10^{-4}$  M) alone was at least a factor of 4 less than Rh 6G, with only a small time dependent change in the probe SH when the pump pulse was not blocked.

From Fig. 1 we note that following photoexcitation of Rh 6G the SH probe signal (which depends quadratically on the probe intensity) initially decreases within the pulse due to a decrease in the nonlinear susceptibility and then more slowly recovers as the excited Rh 6G molecules decay back

to their ground states, where  $E_{2\omega} = \sqrt{I_{SH}}$  recovered with  $\tau = 3.1 \pm 0.2$  ns. When the acceptor DODCI is present the recovery is roughly a factor of 3 faster than when the acceptor is absent, which we attribute to the enhanced deactivation of Rh 6G by energy transfer to DODCI. This threefold change in the interfacial Rh 6G decay is in sharp contrast to the small change in the Rh 6G decay due to DODCI in the bulk medium, as seen by a 17% reduction in the  $3.7 \pm 0.2$  ns bulk decay time (Fig. 2). This is not surprising since the average donor-acceptor distance in the bulk is quite large ( $\approx 130$  Å) at the low concentrations we used. In the interface the relatively strong adsorption leads to smaller donor-acceptor distances. This decreased separation in the interface enhances energy transfer from Rh 6G to DODCI and therefore a more rapid Rh 6G decay. The higher surface concentration of DODCI combined with the stronger donor/acceptor versus donor/donor coupling leads us to at-

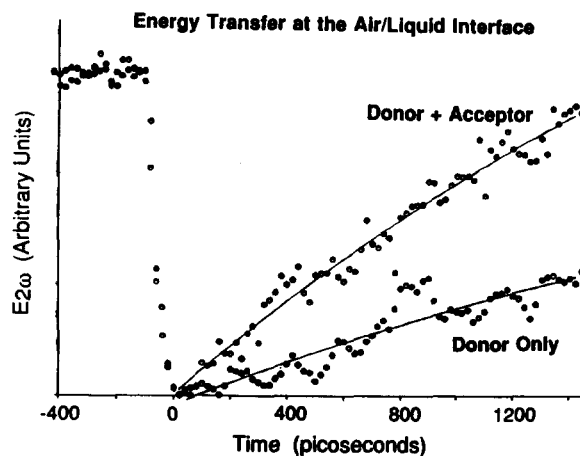


FIG. 1. Effect of energy transfer between the donor Rh 6G (rhodamine 6G) and the acceptor DODCI (3,3'-diethyloxadiazocyanine iodide) at the air/water interface.

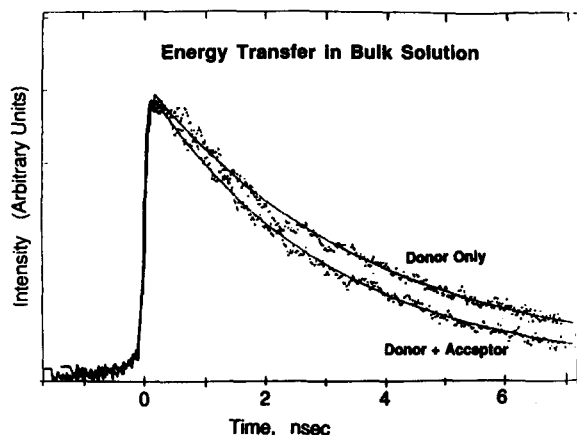


FIG. 2. Effect on the fluorescence decay of the donor Rh 6G ( $2 \times 10^{-4}$  M) by addition of the acceptor DODCI ( $2 \times 10^{-4}$  M).

tribute the energy transfer to direct rather than intermediate donor-donor steps.

Since the energy transfer we are observing by the SH method is from donor to acceptor molecules in the interface, rather than to the much more distant bulk acceptor molecules, we can consider the effect of dimensionality<sup>20-26</sup> on the energy transfer dynamics at the air/water interface. For the singlet-singlet energy transfer process considered in these experiments the nonradiative coupling between excited donor and ground state acceptor molecules is a dipole-dipole interaction, which yields a donor decay of the form

$$D(t) = D(0)\exp[-t/\tau_0 - a_n(t/\tau_0)^n], \quad (1)$$

where  $\tau_0$  is the lifetime in absence of acceptor molecules,  $n$  is 1/2 for three-dimensional energy transfer and yields the usual Förster decay law, and is 1/3 for a two-dimensional transfer.<sup>20</sup>  $a_n$  contains the coupling strength, the orientational factor, and the acceptor concentrations. To fit Eq. (1) to our interfacial data we need to know the relative phase of the excited and ground state donor molecules. In this preliminary report we use opposite phases for them, which can be shown to be an exact fit for a two level system, and thus we have only one adjustable parameter, the coupling strength.

Analysis of the bulk fluorescence in terms of the 3D limit exchange yielded a critical transfer distance of  $\approx 80$  Å. Analysis of the surface SH dynamics yielded reasonable fits for both the 2D and 3D limiting cases. The 3D fit required an acceptor concentration that was four times higher than the bulk concentration, thus indicating that the transfer was in the interface. The fit to the 2D case required the surface

density to be  $\approx 10^{12}$  molecules/cm<sup>2</sup>, which is in the expected range as found for other similarly charged species. Further work is underway to resolve the dependence of energy transfer in the interface on the dimensionality, orientation, and interfacial concentration. In summary, SHG techniques provided the capability to observe the dynamics of intermolecular energy transfer in the air/water interface and thus show that the process was significantly faster than in the bulk liquid.

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