Femtosecond pump-probe spectroscopy for remote sensing of liquid-liquid interface

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This article is dedicated to Prof Pradeep K Gupta for his contributions to optics and photonics with biomedical applications

We report results establishing that detection of the liquid-liquid interface is possible through femtosecond pump-probe spectroscopy. In particular, we use femtosecond laser pulses to pump and probe the dynamics of infra-red dye molecules in a liquid pair that can form an interface. We demonstrate that an interface formation can be detected from such femtosecond dynamical study of the dye molecule. The importance of obtaining the molecular description on the relation between the dynamics of solute molecules and solute-solvent interactions arises from the fact that the dynamic and static properties of dye molecules are strongly affected by the surrounding solvent molecules. © Anita Publications. All rights reserved.

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1 Introduction

Femtosecond transient absorption spectroscopy is a proven technique to study the excited state dynamics of polyatomic molecules. In a typical transient absorption experiment, a molecule is excited by a femtosecond pump pulse to induce a photo-chemical or photo-physical changes. Subsequently, the dynamics of the excited molecule are then observed by recording the absorbance of a weak femtosecond probe pulse as a function of the time-delay between the pump and probe pulses [1]. In such experiments, the pump pulse excites a small fraction of the molecules in the irradiated volume to the higher-energy, photoactive state. To obtain an attractive signal to noise ratio as well as to avoid saturation by the probe, the number of molecules transferred to the photoactive state has to be sufficiently large. Yet, it has to be also small enough to avoid complications from bleaching, etc. and thus, less than 10% of population excitation is often chosen as a rule of thumb for such studies. For systems in the liquid phase (solutions), the study of molecular dynamics with the methodology described above is complicated by the large-bath induced spectral line width and congested vibronic transitions. Additionally, femtosecond pulses typically induce multiple molecular vibronic transitions within the pulse spectral width to hundreds of wavenumbers. The experimental spectroscopic data thus obtained, include contributions from not only the inter-molecular solvent-solute interactions but also the intra-molecular dynamics.

Interfacial regions are boundaries that separate distinct physical and chemical regions of matter. Such interfacial regions exhibit chemical and physical properties that are distinct from the demarcated bulk media. Due to these properties, the interface has fundamental scientific and technological importance. Solvation in bulk liquids has been studied extensively; however, ultrafast dynamics across the interface, where inversion symmetry is broken, has been explored in lesser detail and promising future remains [2,3].

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In this article, we track the interface perturbed molecules near the liquid-liquid interface through the study of femtosecond transient absorption spectroscopy. The femtosecond transient absorption spectroscopy of infra-red dye molecules changes as we move from bulk to the interface. A rigorous understanding of the dynamics of a molecule present in a solvent separated by another solvent by an adjacent layer or interface is crucial in order to obtain information about the dynamics near the interfacial region as a function of distance from the interface. Previous work in this direction has focused on a solvent pair, where the pump-probe signal from the chosen dye was seen in only one of the two solvents forming the interface [2]. Since the dye is miscible in both pure solvents, though the two solvents are not fully miscible with respect to each other, the crossing over of one solvent molecule from one layer to another layer through the interface results in changes in the dynamics of the dye molecule. These changes can be expressed as a function of the distance from the interface [2].

Our present experiments focus on the ultrafast dynamics of a cyanine dye near the interface of a solvent pair, which are mutually not fully miscible. However, the dye characteristics in each of the pure solvents are not drastically different in terms of their excitation features. We demonstrate that the ultrafast pump-probe spectroscopy is still sensitive to the interface. The dynamical behavior corresponds to characteristically distinguishing features of the interface, making it possible to predict the effect of interfaces. Our experiments show that the crossover probability or the penetrating capability of a solute into a solvent is strongly dependent on the parameters like viscosity, dielectric constant and refractive index, etc.

2 Experimental

A cyanine dye, IR775, was obtained from Sigma-Aldrich and was used without further purification. This dye was dissolved in dimethyl sulfoxide (DMSO), and diethyl ether (Et_2O) at a concentration of 5μM. Spectroscopic grade DMSO and Et_2O solvents were used. Electronic absorption spectra of IR775 in DMSO and diethyl ether were recorded against a solvent blank reference with a UV-Vis-NIR absorption spectrophotometer (JASCO, V670) at 0.2 nm resolution using 1 mm optical path length quartz sample cell (Hellma, USA). Femtosecond laser excitation was performed at 800 nm at 1 kHz pulse train of 30 fs pulses (Spitfire Pro, Spectra-Physics, USA, Inc.). Degenerate pump (stronger) and probe (weaker) beams were generated by using an 80:20 beam-splitter (BS). The probe beam (reflected beam from BS) travelled through a retroreflector mounted on a computer-controlled stepper motor translation stage (UTM 150 PP.1, Newport, USA) having a resolution of 0.1 μm. The pump (transmitted from BS) and the probe beams were then combined non-collinearly by using a 10 cm focal length lens. The second-harmonic signal maxima from a BBO crystal (thickness = 0.1 mm) determined the optical zero-delay kept at the focal point of these two beams. The angle between the pump and probe pulse at the focus was kept at ~4°, while the spot size of the pump beam (40 μm) was twice that of the probe beam (20 μm) at the focus. In order to maintain this 2:1 ratio of the pump and probe diameters at focus, the pump power was 100 times higher than that of the probe beam, and the beam diameter of the pump was kept smaller than that of the probe beam.

The dye solution was placed on an XYZ state in a 1 mm cuvette at the same focus as determined by BBO, and the sample was moved along X direction for experimental measurements from the bulk solution to the near interface (Fig 1). The relative transmittance of the probe beam at different X-positions was measured as a function of its delay by using a fast photodiode connected to an oscilloscope interfaced with a personal computer.

The interface between the dye solutions in DMSO with neat-diethyl ether was formed in a 1 mm thin quartz sample cell. We considered the interface to be a planar region defined by X = 0, which corresponds to the region devoid of probe signals due to strong scattering. For our experiment, we moved the sample cell along the X-axis, as is shown schematically in Fig 1. We define X = 0 to be the interface; a positive value of

X (X > 0) corresponds to the Dye solution in DMSO and negative values of X (X < 0) correspond to the neat-diethyl ether phase. All these experimental data were recorded at room temperature (295K). Earlier studies have shown that the ultrafast dynamics of a popular indocyanine-green dye (IR125) in dichloromethane (DCM) solvent is a strong function of the distance from its interface that is formed with a pure water layer [2]. In our present degenerate pump-probe experiment, for studying the effect of the interface of two not fully miscible solvents, we have chosen IR775 in DMSO solution interfaced with pure diethyl ether. The absorption spectra of IR775 in DMSO and diethyl ether solution shows that the central wavelengths of the absorption maxima in DMSO and diethyl ether are 792 and 791 nm, respectively (Fig 2).
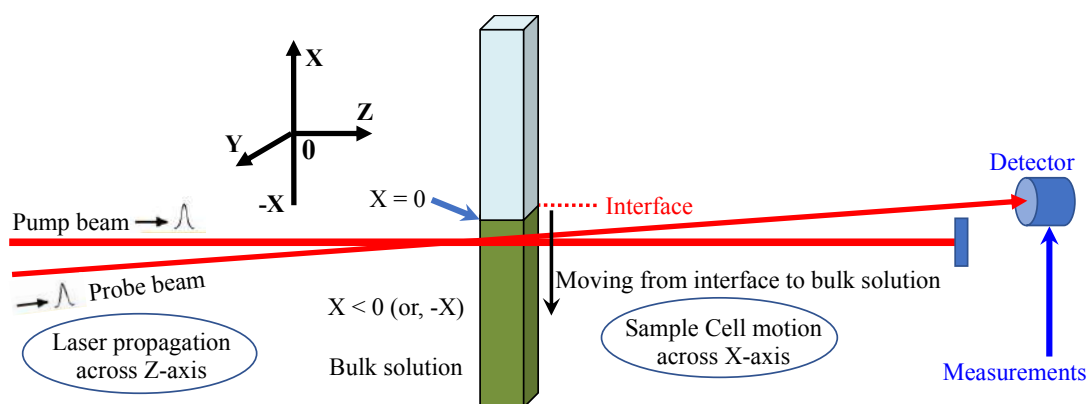

Fig 1. Schematic representation of our experiments showing femtosecond laser propagating along the Z-axis for degenerate wavelength pump-probe measurement across the liquid-liquid interface by moving the sample cell along the X-axis.
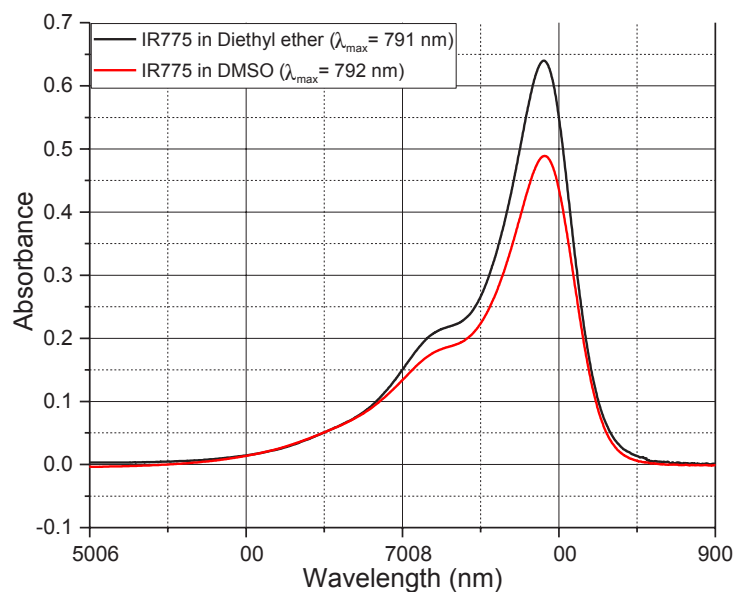

Fig 2. Absorption spectra of IR775 in DMSO and diethyl ether solvents. Despite the difference in solvent characteristics, the spectral features are quite similar, and the peak shift is 1 nm.

The shoulders in the higher energy region of the absorption spectra are due to vibronic side band coupling. A similar type of vibronic side band coupling of the same dye in different solvents and binary mixtures have been observed and reported in the literature by our group [4]. These two solvents are chosen to emphasize the effect of extreme solubility of the dye molecules in both solvents. The selected solvents also show a desirably large viscosity difference at room temperature, which does not allow them to be miscible, and diethyl ether floats on DMSO. We always worked with a fresh interface generated by carefully adding the neat diethyl ether added to the carefully made and preserved 5 μm IR775 dye DMSO solution. Given that the dye is highly soluble in both the solvents, a freshly prepared sample ensured that the partitioning of the dye across the interface remained the same throughout our repeated experiments. Our experiments were always completed within half an hour of generating the interface sample.

3 Results and Discussion

The ultrafast dynamics resulting from the degenerate pump-probe studies of the IR775 dye in DMSO interfaced with neat-diethyl ether as a function of distance (X, in mm) from the interface is depicted in Fig 3. From a distance of 0.6 mm from the interface, as we move towards the dye solution in DMSO, there are no further changes in the observed dynamics, indicating that bulk conditions apply beyond this distance from the interface.
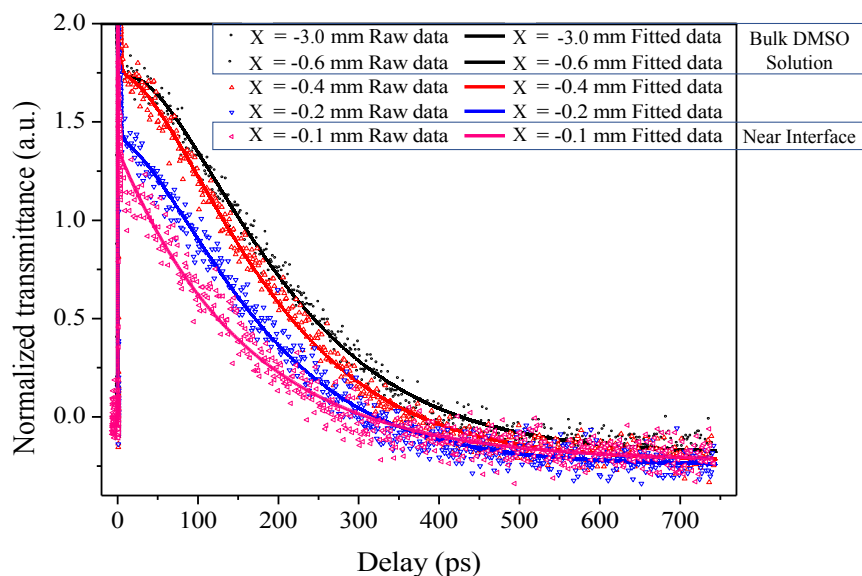

Fig 3. Degenerate pump-probe spectra of IR775 in DMSO at different X-positions from bulk DMSO solution to near the DMSO-neat–diethyl ether interface. Symbols of different colours represent raw data, while solid lines with the corresponding colour indicate the best fit (Dye Concentration 5×10^{-6} M).

We used a multi-exponential decay function to fit the experimental time-resolved traces obtained from the pump-probe experiments. The decay time constants of our experiments are tabulated in Table 1 with their respective amplitudes. A close inspection of Table 1 reveals two types of distinct dynamics; the first set appears on moving from X = 0.6 mm to X = 0.2 mm, and the second at very near the interface, X = 0.1 mm.

We assign τ_1 as a coherent artifact [2,4]. The value of τ_1 remained almost constant during the entire measured dynamics at different X positions. The second decay τ_2 was identified to be the vibrational cooling (VC) time, which controls the heat dissipation processes from the hot solute molecules to the surrounding

solvent layers [4-11]. The third and fourth decay time constants τ_3 and τ_4 were assigned to the intermediate state time and ground state recovery time, respectively. A careful observation indicates that after vibrational cooling, there is a growth phase followed by ground-state recovery. This growth in the time-resolved traces is a clear indication of the formation of an intermediate state [11-14]. The intermediate state formed in our experiments is the main reason underlying the observed growth in time-resolved traces and is formed from the hot ground molecules. The intermediate state becomes stable due to electron donation from the nitrogen atom through the skeleton of the dye as a result of electron delocalization and is shown in Fig 4.

Table 1. Decay time constants for the degenerated pump-probe spectra at different X-positions.

X (mm)	a_1	τ_1 (fs)	a_2	τ_2 (ps)	a_3	τ_3 (ps)	a_4	τ_4 (ps)
0.6	0.05	34	0.12	2.10	0.39	104.30	0.44	120.30
0.4	0.04	34	0.10	2.42	0.41	97.30	0.45	105.30
0.2	0.04	38	0.9	2.53	0.42	93.30	0.45	101.60
0.1	0.12	40	0.15	0.67	--	--	0.73	165.00

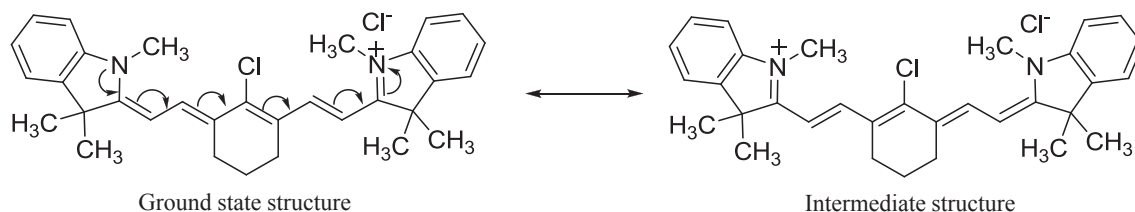Ground state structure   Intermediate structure

Fig 4. Intermediate structure of IR775 dye.

The vibrational cooling time increases and the intermediate state time decreases as we moved from 0.6 mm to 0.2 mm with respect to the interface, indicating that the system becomes more heterogeneous at 0.2 mm compared to 0.6 mm relative to the interface. Consequently, the vibrational cooling time increases near the interface, at position 0.2 mm (from the interface), compared to at position 0.6 mm (from the interface). The intermediate state time decreases as we moved from bulk to near the interface (0.6 mm to 0.2 mm with respect to the interface). We did not observe any growth in the time-resolved trace at X = 0.1 mm (near the interface), indicating that the intermediate state is not formed at X = 0.1 mm. Near the interface (X = 0.1 mm), the penetration probability of neat-diethyl attains its maximum value, and due to the low viscosity of diethyl ether, we argue that the deactivation channel through the intermediate state formation is blocked. Thus, the ground state decay dynamics is only observed near the interface (0.1 mm). This signifies that our results show that the concentration of DMSO plays a critical role in the formation of the intermediate state. In bulk (X = 0.6 mm), as the concentration of DMSO present is maximum, the intermediate state is more strongly present.

Furthermore, the high viscosity of DMSO plays an important role in the formation and stabilization of the intermediate state (Fig 4). DMSO is a highly polar aprotic solvent, while diethyl ether is hydrophobic [15]. On moving from the interface of the DMSO solution with the neat-diethyl ether layer into the bulk DMSO solution, the penetration of diethyl ether decreases. The maximum penetration of diethyl ether into the bulk DMSO layer occurs near the interface (in our experiments, this corresponds to X = 0.1 mm) and is shown schematically in Fig 5. This is attributed to the very high viscosity of DMSO (2.14 cp at 20°C), which is ~9 times higher than the viscosity of diethyl ether (0.2448 cp at 20°C). Due to this viscosity variation, the penetration of diethyl ether is increasingly restricted as we approach the bulk dye solution in DMSO from the interfacial region.
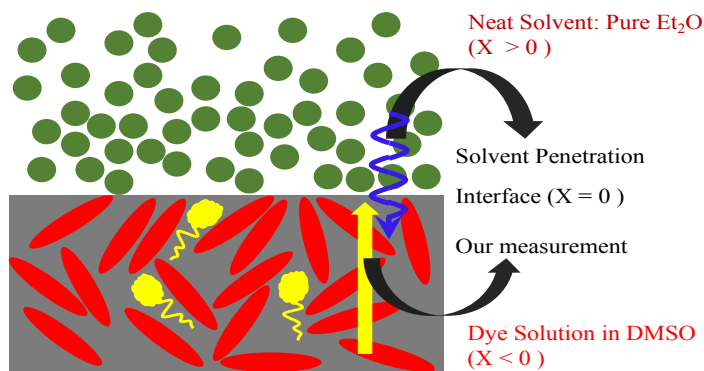
Fig 5. Schematic representation of the penetration of pure diethyl ether into the dye solution in DMSO through the interface across the two solvents.

Figure 6 shows further effects of the viscosity difference. The retardation of the penetration probability creates a spatial heterogeneity due to which, the viscosity at X = 0.1 mm becomes lower compared to that on moving from X = 0.2 mm to X = 0.6 mm as shown in Figure 6.
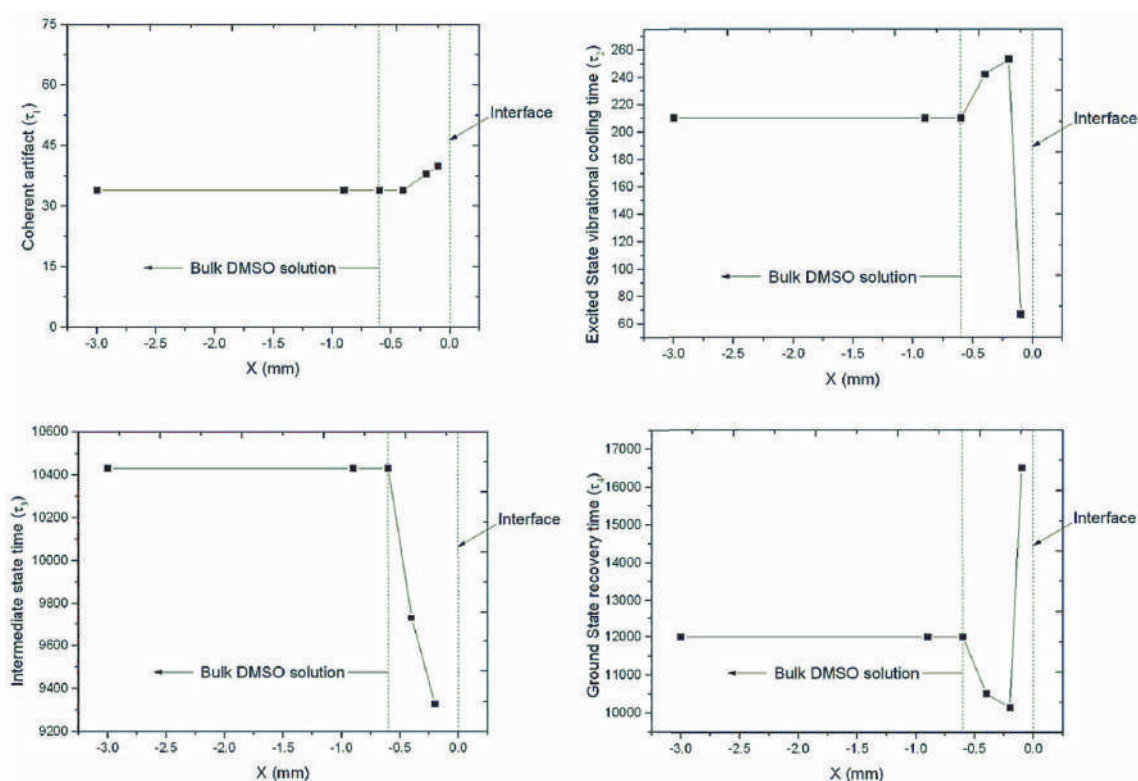

Fig 6. Variation in the different lifetime components of the multi-exponential fit to the experimental time-resolved traces.

We establish from our experiments and from the multi-exponential fit variations (Fig 6) that as we move closer to the interface, the decay time constants start changing, bolstering the assertion that, as

compared to the bulk, interface dynamics are quantitatively different near the interface. These distinctive changes in character in the vicinity of the interface allow for sensitive measurements to infer the presence of an interface remotely even when not sampling at the exact interface.

4 Conclusion

The vibrational cooling time depends on the locations of excitation and shows maximum at X = 0.6 mm and becomes progressively lower on approaching the interface because, on moving from bulk to near the interface, the penetration of diethyl ether reduces. The intermediate state time is higher at X = 0.6 mm compared to X = 0.2 mm, while at X = 0.1 mm, we do not observe any intermediate state. The drastic changes in the decay constants near the interface, X = 0.1 mm, occur due to the maximum penetration of diethyl ether into the DMSO layer near the interface as a result of spatial heterogeneity. This study indicates that solvent penetration strongly affects the viscosity of the solution at different positions if the two solvents with high viscosity differences are separated by an interface and such a study can then be used to sense the interface

Acknowledgments

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