ADVANCED LASER SPECTROSCOPY AT BULK AND INTERFACES

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Abstract

Understanding the physicochemical properties and excited-state dynamics of molecules at bulk and interfaces is of essential importance in fundamental sciences and applied fields. Advanced laser spectroscopy techniques such as, heterodyne-detected vibrational sum frequency generation (HD-VSFG) and femtosecond transient absorption spectroscopy revealed important interrelations between the physicochemical properties/excited-state dynamics of molecules and their functional groups and properties of bulk and interfacial media.

Introduction

Photoinduced intra-/intermolecular processes (electron/energy transfer, conformational/configurational changes, etc.) are vital in many natural (e.g. photosynthesis, vision, phototropism) and artificial (photovoltaics, molecule-based electronics, etc.) systems.[1] In general, absorption of UV-Vis. photon lands a molecule on an excited potential energy surface, which while relaxing to the ground-state, undergoes electron/energy transfer or conformational/configurational changes in an extremely fast rate ($\sim 10^{12}$ s$^{-1}$). By using femtosecond transient absorption spectroscopy, we directly monitored the excited electronic states of various model molecules and unravel the role of functional groups and the properties of bulk solvent media on various photoinduced processes. Previous studies indicated that interfacial chemistry, which plays important roles in chemistry (solvent extraction, food technology, catalysis), biology (cell membrane interface), and environmental sciences is different from bulk phase chemistry. Nevertheless, because of the technical difficulty of selectively probing of an interface ($\sim$ a few nm thick), the molecular level understanding of interfacial phenomena is limited. Very recently, we applied heterodyne-detected vibrational sum frequency generation, HD-VSFG[2] to selectively probe the vibrational characteristics of molecules located at a few molecular layer thick interfaces. Our HD-VSFG investigations revealed unique organization of water at cationic, anionic, and zwitterionic lipid containing cell membrane-water interfaces.

Excited-state dynamics of photoinduced processes in bulk liquid phase

Intramolecular electronic energy transfer (EET) in bichromophoric molecule.

In some bichromophoric molecules, the energy levels of the two chromophores, although not perturbed significantly by each other, are coupled enough to participate in rapid non-radiative energy transfer from the excited-state of one chromophore (donor) to the other (acceptor). We investigated the EET dynamics in a special kind of bichromophoric molecule, (2-(9-anthryl)-1H-imidazo [4,5-f] [1,10]-phenanthroline (AIP)) whose donor (anthracene (AN)) and acceptor (1H-imidazo [4,5-f] [1,10]-phenanthroline (IP)) groups are directly linked. Thus, the donor and acceptor groups in AIP are very short distance (one $\sigma$ bond) apart (Figure 1). Transient absorption studies showed that the rate of energy transfer decreases with increasing viscosity of the medium.[3] This means the energy transfer in
such directly linked bichromophoric molecule is accompanied by conformational change, which is required for the efficient orbital overlap in the EET process.

Fig.1: Intramolecular-EET in AIP (from anthracene to imidazophenthroline). Because the donor and acceptor groups are directly linked in AIP, the rate of EET is inherently fast ($1.8 \times 10^{11}$ s$^{-1}$ in methanol) and depends upon the relative orientation of anthracene and imidazophenthroline moieties in the photoexcited state.

Intramolecular charge transfer (ICT) in donor-acceptor molecules.

Like the energy transfer in bichromophoric AIP, a molecule with two types of functional groups— one electron rich and the other electron deficient, can undergo ICT on photoexcitation. We investigated the ICT dynamics in several electron donor-acceptor molecules (e.g. Michler’s ketone (MK), 2-dimethylamino-7-nitrofluorene (DMANF) and 4-(N,N-dimethylamino)-4′-nitrostilbene (DMANS); Figure 2a) in different bulk liquid phases. In Michler’s ketone (MK), for example, the electron donating N,N-dimethylanilino groups are attached with an electron withdrawing carbonyl group and because of the steric hindrance, the two N,N-dimethylanilino groups are not in the same plane (pre-twisted in ground-state). On 400 nm photoexcitation, the pre-twisted locally excited S$_1$ state undergoes two consecutive conformational relaxation processes. First, an ultrafast anti-twisting motion of the dimethylanilino groups takes the molecule to a near-planar geometry with high mesomeric interaction (ICT-state). Then, in highly polar solvents, the N,N-dimethylamine groups (-N(CH$_3$)$_2$) undergo $\sim$ 90$^\circ$ twisting with respect to their phenyl rings. This leads to the conversion of the intermediate ICT-state to a highly polar twisted intramolecular charge transfer (TICT) state.[4] To look into the intricacies of the excited-state ICT and twisting processes, we investigated 2-dimethylamino-7-nitrofluorene (DMANF) where the ‘dimethylanilino-like’ electron donor and ‘nitrophenyl-like’ acceptor groups are rigidly bonded (not free to twist). It is observed that in the case of DMANF, the nitro group is twisted to accommodate the charge in the lowest energy excited-state. Thus, unlike in the well-studied dimethylamine benzonitrile[1] where the electron donating N,N-dimethylamino (-N(CH$_3$)$_2$) is twisted, it is the electron accepting nitro group that is twisted in the excited-state of DMANF.[5] In fact, we found that it is the electron donating and accepting ability of the donor and acceptor groups that determines the site of conformational change in a molecule.

Fig.2: (a) Chemical structures of different molecules used in photoinduced charge transfer and conformational/configurational relaxations studies. MK: Michler’s ketone; DMANF: 2-dimethylamino-7-nitrofluorene; DMANS: trans-4-(N,N-dimethylamino)-4′-nitrostilbene. (b) Typical role of solvent properties on the TICT dynamics: in less polar solvent, the TICT is activation barrier controlled and in highly polar solvent it is governed by the viscosity of the medium.
Donor-acceptor molecules in which the electron donor and acceptor groups are separated by long conjugations are active ingredients of optoelectronic and molecule-based devices. However, the additional conjugations (mesomeric bridge between the donor and acceptor) are likely to provide potential deactivation pathways to the excited states that may have adverse effect on the desired photo-processes. Investigations of the dynamics of trans-4-(N,N- dimethylamino)-4'-nitrostilbene (DMANS), which has a C=C bond in between the donor (N, N-dimethylanilino) and acceptor (nitrophenyl) groups, showed different behavior in different solvents. For example, in nonpolar cyclohexane, it undergoes photoisomerization whereas, in polar acetonitrile, TICT is the dominant relaxation processes in the excited-state. Moreover, the rate of formation of the TICT state increases exponentially with the polarity of moderately polar solvents (ETn < 0.3), which signifies a solvent (polarity) dependent activation barrier for the TICT process. Nevertheless, in highly polar solvents (ETn > 0.4), the activation barrier is negligible and the rate of TICT depends on frictional interaction (viscosity) with solvents (Figure 2b).[6]

Photoisomerization in azo-compounds:

Photoinduced isomerization is an important elementary process in liquid crystals, optical switching, memory storage, and photoregulation of biofunctions. As a result, extensive researches were carried out to understand the photoisomerization dynamics of azobenzene and related compounds. Using transient absorption spectroscopy, we investigated the photoisomerization dynamics of a different class of azo-compounds (N-1-methyl-2-(tolylazo) imidazole (MTAI)) and its metal complexes (Figure 3). From time evolution of the transient spectra and global analysis of the temporal proles, it has been observed that isomerization occurs in the S1 state of MTAI via the inversion at one of the azo-nitrogen atoms.[7] However, on complexation with Cu(II), [Cu(trans-MTAI)]Cl2, the photoinduced isomerization of the azo-backbone is inhibited.

Physicochemical properties of water at model membrane/water interfaces

An interface is a common boundary across two immiscible bulk phases and has properties that are different from either of the bulk phases. As a consequence, chemistry at interface is different from that in bulk of a medium. Recently, we have demonstrated distinct properties of water at model membrane/water interfaces by using a novel HD-VSFG technique.[8] Measurement at different charged and zwitterionic lipid monolayer/water interfaces revealed unique organization of water at membrane interfaces (Figure 4). For instance, at charged lipid interfaces, water is preferentially oriented by the interfacial electric field created by the charge on lipid headgroups.[9] Water takes H-up (water dipole is pointed toward the lipid phase) orientation at negatively charged interfaces and H-down (water dipole is pointed toward the aqueous phase) orientation at positively charged lipid interfaces. On the other hand, at the net neutral zwitterionic lipid (phosphatidylcholine) interface, water takes a net H-up orientation. This means that the anionic phosphate has stronger water orienting ability than that of the cationic choline in phosphatidylcholine. In fact, there are distinct water structures around the...
phosphate and choline groups. [10] In general, interfacial water is more inhomogeneous than the bulk water and there is very weakly or non-H-bonded water species at lipid interfaces.


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References

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