8.1. Summary of the Work:

In the preceding chapters we have discussed our work on three double molecules. In Chapter V, we have discussed our work on the geometry change in the triplet state of a labile double molecule, \(\alpha\)-naphthil. In Chapter VI, we have described our work on the characterisation of fluorescence from relaxed and unrelaxed state of another labile double molecule, benzil. In Chapter VII, we have discussed the detection of the level splitting of a rigid double molecule, trans-acenaphthylene dimer (TAD) and the assignment of the split electronic energy levels.

8.1.1. Conformational Relaxation in the Excited Triplet of \(\alpha\)-Naphthil:

In case of \(\alpha\)-naphthil, the 'relaxed' triplet has a well characterised emission band at 580 nm. We, therefore, studied the dynamics of the geometry change in the triplet state by following the time development of the 580 nm band after excitation by a nanosecond pulse. At ambient temperature,
in fluid solution the molecular motion involved in the geometry change is very fast and is detectable using only picosecond methods. We have, however, shown that if a clever choice of conditions is made this ultrafast process can be slowed down to a great extent. Thus we have observed this process in a highly viscous medium at low temperature (namely, semisolid glass, a few degree below mp) using a nanosecond laser and a microsecond detection electronics. Our time resolved study revealed that in semisolid glass the decay of the 580 nm band of α-naphthil is preceded by a growth. This viscosity-dependent growth gives a conclusive evidence in favour of the proposition that in fluid media α-naphthil undergoes a geometry change from unrelaxed skew ππ* triplet to relaxed trans-planar nπ* triplet. We have analysed our kinetic results qualitatively in terms of a simple kinetic scheme. It is apparent that with rise in temperature as viscosity of the semisolid glass decreases the rate of the torsional motion should increase. According to our kinetic scheme, this should be reflected in a shortening of rise time of the relaxed phosphorescence. Our results are in qualitative agreement with this speculation. In comparison to benzil, in which similar geometry change is known to occur, the torsional motion should be slower for α-naphthil, as in the latter the two rotating halves are more bulky. Moreover, since the unrelaxed triplet state of benzil is a nπ* triplet while
that of \(\alpha\)-naphthil is a \(\pi\pi^*\) triplet, the life time of the unrelaxed state in case of \(\alpha\)-naphthil is longer. Our kinetic scheme predicts that the relatively slower rate of torsional motion and the longer life time of unrelaxed triplet should result in a longer rise time in case of \(\alpha\)-naphthil compared to that of benzil under similar conditions. This prediction has also been confirmed by our experimental results.

8.1.2. Fluorescence from Relaxed and Unrelaxed Excited States of Benzil:

At low temperature in rigid glass, the life time of the \(n\pi^*\) singlet state of benzil is very much smaller than that of triplet state. As a result the time integrated intensity of \(n\pi^*\) fluorescence is much smaller than that of phosphorescence and the latter almost completely masks the former. This is the reason of the difficulty in observing \(n\pi^*\) fluorescence at low temperatures. We have demonstrated that the short lived fluorescence can be extracted out from the intense background of long lived phosphorescence by the Boxcar gating technique. In this method we have used an aperture duration much shorter than the life time of the intense phosphorescence which ensured that only the short lived fluorescence of a much higher
instantaneous intensity has been sampled. Using this method we have detected a new emission band of benzil, which exhibits mirror image relationship with absorption and blue shift in polar solvent relative to the emission in crystal. These facts and the short life time (~10 ns) have led us to assign this new emission as the fluorescence from the unrelaxed, skew, \( n^* \) excited state of benzil. From the comparison of intensities of the unrelaxed fluorescence (at 450 nm) and relaxed fluorescence (at 505 nm) in alcohol as a function of temperature we have concluded that the relaxed fluorescence dominates over the unrelaxed fluorescence at a temperature above melting point of the glass. The dominance of the relaxed fluorescence over unrelaxed fluorescence is an indication that above mp of glass, the geometry change occurs in the \( S_1 \) state as well. We have earlier found that the geometry change in the triplet state (as is evidenced by the growth and decay of relaxed phosphorescence) occurs at a temperature 15-20° below mp of the glass. We have shown that in softened glass (i.e. 15-20° below mp) the rate of geometrical relaxation (1.56x10^4 sec\(^{-1}\)) is fast enough to occur within the lifetime of triplet state of benzil but is too slow to occur in the lifetime of the unrelaxed excited \( S_1 \) state. We have observed that while the absorption and unrelaxed emissions of benzil show a marked blue shift in polar solvent (alcohol) relative to a non polar
solvent (methyl cyclohexane), the relaxed emissions show little or no such solvent shifts. This lack of solvent shift has been interpreted by us as an indication of the trans planar geometry of the relaxed excited state of benzil in which both the excited and ground state has zero dipole moment and hence there is no difference in polarity between them.

8.1.3. Level Splitting in trans-Acenaphthylene Dimer:

To study the level splitting in double molecule we have chosen a rigid double molecule, trans-acenaphthylene dimer, in which two naphthalene rings are held at close distance by a cyclobutane ring. Thus this system is analogous to two naphthalene molecules in the unit cell of naphthalene crystal. In analogy to the exciton splitting in naphthalene crystal, we expected the splitting to be small in case of TAD. Since our attempts to grow single crystals of TAD of good quality and to dope it in several hosts failed, we could not study the high resolution spectra in single crystals. We, therefore, decided to make use of the Sphol'skii effect to get quasilinear spectra. Our system (TAD) gave quasilinear emission and excitation spectra at 77°K in polycrystalline n-octane medium (Sphol'skii matrix). The complete lack of mirror image relationship between the excitation and the emission spectra of TAD indicated presence of two close lying electronic energy
levels. We have shown that the emission spectrum can be interpreted as two interlocking band systems with origins at 31125 and 31055 cm\(^{-1}\). These two origins have been interpreted by us as the two excitonic states of the double molecule of splitting 75 \(\pm\) 10 cm\(^{-1}\), both of which are populated at 77\(^{0}\)K. The high resolution excitation spectra in Sphol'ski matrix gave the splittings of the different vibronic levels. We have shown that the splittings of the vibronic levels are roughly proportional to the intensity of the respective vibronic bands, which is consistent with the exciton theory in the weak coupling case. Since our system is centrosymmetric, the excitonic states can be classified as 'g' and 'u' states. To identify the symmetry of the split energy levels we compared the one- and two-photon spectra around the "vibrationless" origin. From this we concluded that the states at 31025 cm\(^{-1}\) and 31125 cm\(^{-1}\) respectively correspond to the g and u symmetry. We have shown that our results are in qualitative agreement with the simple exciton model. The lack of quantitative agreement may be due to the "through bond" interaction between the two halves. We also tried to study the high resolution phosphorescence spectrum of TAD, but failed to detect it because of the weakness of the phosphorescence. The weakness of the phosphorescence led us to
suspect some photochemical reaction occurring in the triplet state of TAD. Subsequently, through energy transfer experiments we proved that the photochemical decomposition of TAD intoacenaphthylene monomers proceeds via the triplet state of TAD.

8.2. Extensions of the Work in Progress:

8.2.1. We have pointed out that our kinetic data on the photodynamics of α-naphthil in triplet state could not be analysed quantitatively because in a semisolid glass different regions may have different viscosities and consequently different rate constants. A quantitative study can, however, be made if the growth and decay of the relaxed phosphorescence are observed in a medium of uniform viscosity e.g. in fluid solution at ambient temperature. The detection of growth and decay under these conditions involve picosecond techniques. About four years back, when we first observed these growth and decay of relaxed phosphorescence we did not have the picosecond set up in our laboratory. At present we are setting up our picosecond laboratory to extend these studies into the picosecond domain. We have also found that similar geometry change occurs in the excited singlet state of benzil at a temperature above melting point of glass. We expect that under this condition the relaxed fluorescence will also exhibit a growth followed by a decay in a time scale of picoseconds.
8.2.2. Encouraged by our success in observing the intramolecular exciton splitting in a rigid double molecule separated by multiple chains of two saturated C atoms, we have recently chosen another rigid double molecule in which two benzene rings are separated by a single C atom. Our preliminary results indicate that the splitting is quite large ($\approx 500 \text{ cm}^{-1}$) so that emission originates from only one of the split levels. From the comparisons of one- and two-photon spectra we have also detected a g-state located below the one-photon allowed u state. Details of this study will be discussed elsewhere.