PICOSECOND KINETICS OF EXCITED CHARGE-TRANSFER INTERACTIONS

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The geometrical requirements and effects of solvent polarity on excited-state charge-transfer processes are investigated using picosecond laser methods. For the model compound anthryl–$(CH_2)_3$–N,N-dimethylaniline the dynamics of both forward and back electron transfer in polar and nonpolar solvents are presented.

1. Introduction

One of the key processes by which organic molecules in excited electronic states degrade their electronic energy is by charge-transfer interactions between the excited molecule and surrounding ground-state molecules. The transfer of an electron from a ground-state donor molecule D to an excited acceptor molecule A^* quenches the normal fluorescence of A^*, leads to the appearance of a new emission in low dielectric solvents, can produce ion radicals in polar solvents, and can change the chemistry of the system. Since the discovery of excited-state charge-transfer complexes by Leonhardt and Weller [1], the physical and chemical nature of these diverse processes have been extensively studied [2–9]. Investigations, especially on anthracene (excited-state acceptor A^*) and N,N-diethylaniline (ground-state donor D) have yielded information about the nature of diffusion-controlled reactions in liquids, orientational relaxation of the charge-transfer complex $(A^-{-}D^+)^*$, energy dissipation in the complex, and an estimate of the electron-transfer jump distance.

To determine the role of geometrical effects on the dynamics of the electron-transfer process the acceptor anthracene was linked to the donor dimethylaniline via three methylene groups, $A{-}(CH_2)_3{-}D$, as was initially done by the Weller group [10], Chandross and Thomas [6], and Mataga and co-workers [5]. It has been found for this model compound that the emission in low polarity solvents consists of a red-shifted structureless charge-transfer emission as well as an anthracene type emission. In highly polar solvents there is no emission observed for this model compound which is consistent with the view that solvated radical ions A^- and D^+ are formed rather than the $(A^-{-}D^+)^*$ complex found in nonpolar solvents. In this work the dynamics of the electron transfer from D to A^* and subsequent decay processes in nonpolar and polar solvents are reported.

2. Experimental

A single laser pulse was extracted from the train of pulses generated by a mode-locked ruby laser and was frequency doubled from the fundamental at 0.6943 μ to 0.3472 μ. The 0.3472 μ pulse was then used to excite the ^1L_a state of anthracene. The fundamental frequency of the laser at 0.6943 μ, resonant with the $A^{\cdot -} \rightarrow A^{\cdot -*}$ transition, is used to probe the electron transfer up to 1200 ps after the 0.3472 μ excitation pulse. Polarization measurements were used to separate changes in absorption due to the population growth in $(A^-{-}D^+)^*$ or A^- from absorption changes due to orientational redistribution [7]. The width of the laser pulse was about 10 to 15 ps. The optical arrangement is shown in fig. 1. The preparation of the compound is described in ref. [11].

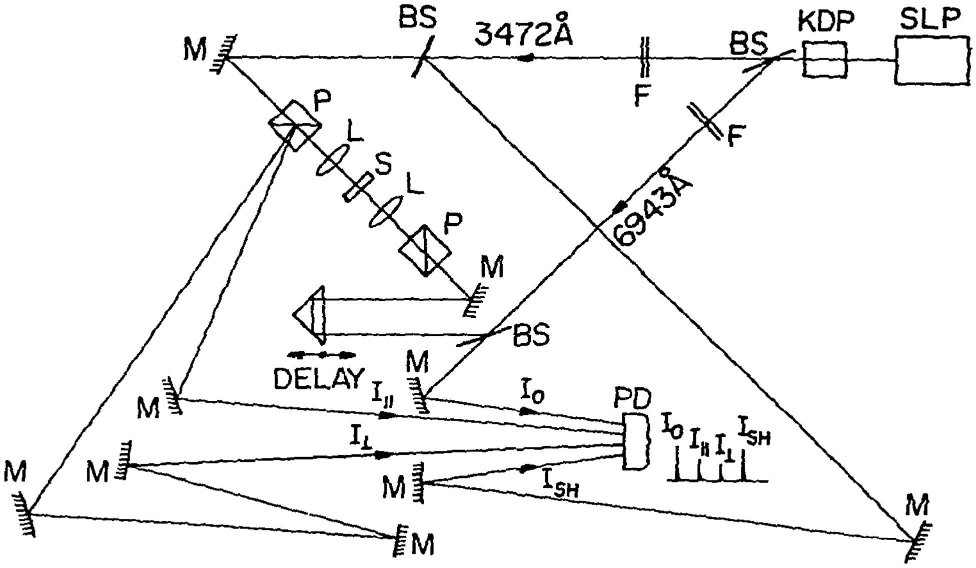

Fig. 1. Optical arrangement for monitoring $I_\parallel$ and $I_\perp$ transmissions at 6943 Å following the photoexcitation by a second-harmonic (3472 Å) pulse (I_{SH}). (SLP) single laser pulse at 6943 Å from the laser oscillator, single pulse selector and laser amplifier systems; (KDP) second harmonic crystal; (BS) beam splitter; (F) filter; (M) mirror; (P) polarizer; (L) lens; (S) sample; (PD) photodiode.

3. Results and discussion

In the solvent hexane the electron transfer from D to A* is initially rapid, leveling off or increasing very slowly after 40 ps, fig. 2 ‡. The number of charge-transfer complexes formed in the linked molecule is significantly less, by roughly a factor of four, than for the free system at a high concentration of D, as estimated from absorption measurements. A possible explanation of the diminished complex formation for the linked molecule would be the requirement for the D and A* moieties to rotate into some overlapping sandwich configuration for electron transfer to occur. If the time required for the rotation about the methylene groups into a favorable geometry is longer than the lifetime of A*, then only some fraction of the A*–$(CH_2)_3$–D molecules will achieve this configuration before the A* decays back to the ground state. If rotation of the D and A* during the lifetime of the A* is important then the dynamics and number of charge-transfer complexes formed should be viscosity dependent. Thus in a more viscous solvent such as hexadecane the charge-transfer process should be impeded relative to hexane due to the increased time required for the rotation of the D and A* groups into the favorable geometry. (At room temperature the viscosity of hexadecane (3.34 cP) is ten times greater than that of hexane (0.33 cP) and their dielectric constants are about the same, $\epsilon \approx 2$.) As shown in fig. 2 the rate of formation of the charge-transfer complex and the number of charge-transfer complexes formed are the same in hexadecane and hexane.

These results suggest that in the ground state approximately one fourth of the A–$(CH_2)_3$–D molecules in both hexane and hexadecane are in a sandwich configuration, as limited by the methylene groups, with the remaining molecules having the A and D in a non-overlapping extended configuration. On excitation of the A portion, an electron is transferred from D to A* only for those molecules in the overlapping configuration. The rapid rise in about 40 ps is attributed to the electron transfer occurring in those molecules having this favorable configuration. For the molecules in the extended configuration there is negligible electron transfer since the A* decays (5.5 ns) before the D and A* portions can rotate about the methylene

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‡ This result is contrary to previous findings [11], a discrepancy which is attributed to degradation of the sample used in the earlier work.

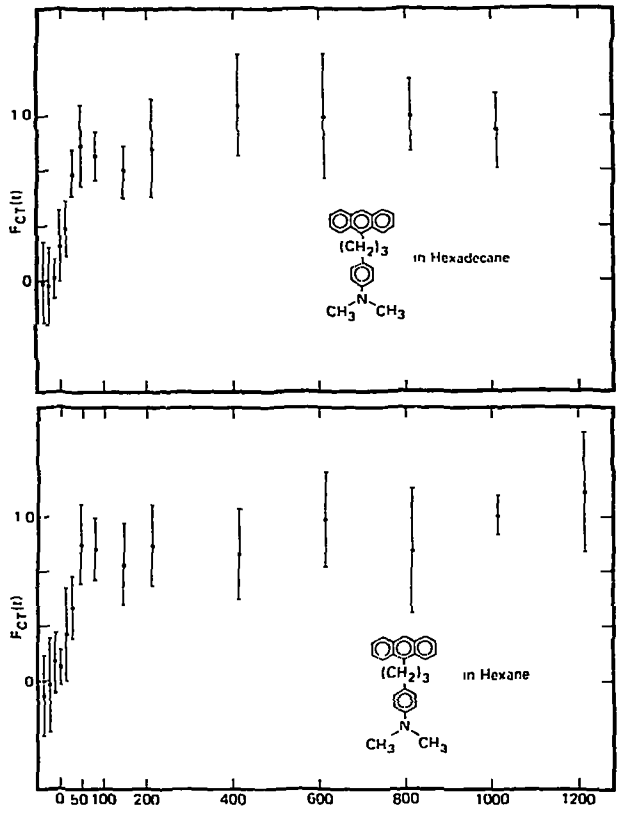

Fig. 2. Normalized population, F_{CT}, of charge-transfer species as a function of time on excitation of $A{-}(CH_2)_3{-}D$ in hexane and hexadecane.

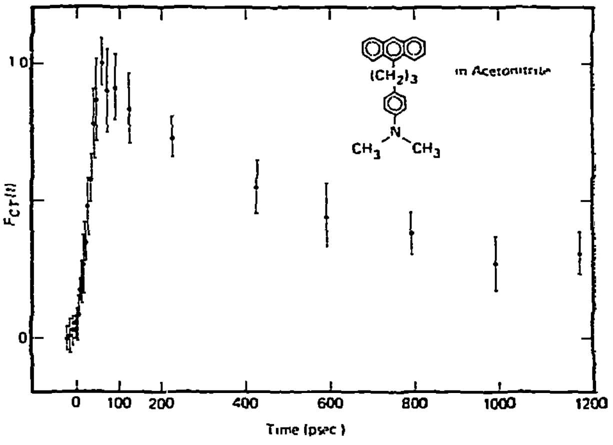

Fig. 3. Normalized population, F_{CT}, of charge-transfer species as a function of time on excitation of $A{-}(CH_2)_3{-}D$ in acetonitrile.

groups to the configuration favorable for electron transfer. The observation of the fluorescence from the anthracene portion of the linked molecule in hexane [5] with a decay time of 5.5 ns is consistent with this interpretation of the picosecond measurements.

It is therefore concluded that there are strong geometrical requirements for electron transfer in the non-polar (low dielectric) solvents hexane and hexadecane, and that the rotation of D and A* about the methylene group to a favorable geometry has a time constant in excess of 5 ns in these solvents.

The time evolution of the electron-transfer process in the $A{-}(CH_2)_3{-}D$ molecule in the high dielectric solvent acetonitrile is shown in fig. 3. As with the low dielectric solvents the initial rise is rapid and peaks in about 40–50 ps after the excitation pulse. However, the amplitude of the effect is larger in the high versus low dielectric solvents and is comparable to that of the unconnected donor and acceptor at a high donor concentration. This again is consistent with the observation of almost complete quenching of A* type fluorescence of the linked molecule in acetonitrile [5]. Subsequent to the rapid rise a marked decrease of the absorption with time is observed, initially decaying with a time constant of 760 ± 80 ps. We attribute this to fast intersystem crossing from $A^{\cdot -}{-}(CH_2)_3{-}D^{\cdot +}$ to ${}^3A^*{-}(CH_2)_3{-}D$, i.e. to the triplet state of anthracene and the ground state of the donor. This interpretation is in agreement with the observation of the appearance of triplet–triplet absorption bands $T_1 \rightarrow T_n$ within a time delay of 600 ps to 5 ns for the unlinked system in acetonitrile [10]. A similar curve with the same rise-time and amplitude is found in the solvent methanol, where a similar long time decay was indicated to the longest measurement time of 125 ps.

The higher amplitude of the electron-transfer process in the high dielectric solvents can be due to the ground-state molecules $A{-}(CH_2)_3{-}D$ preferring an overlapping configuration. This configuration is favorable for electron transfer on excitation of A to A*. Packing effects due to molecular shapes and sizes as well as strong solvent–solvent polar interactions could favor the more compact configuration of $A{-}(CH_2)_3{-}D$ in the acetonitrile and methanol solvents, thereby minimizing the disruption of the solvent structure. Another possibility for the larger effect in the polar solvents is the relative shifting of the

$A^*-(CH_2)_3-D$ and $A^{\overline{\cdot}}-(CH_2)_3-D^{\dot{+}}$ energy surfaces due to solvation. This could lead to a substantial increase of the electron-transfer probability for the extended configuration in the polar solvents.

Further experiments on the role of the solvent in the formation and decay of excited-state charge-transfer complexes and radical ions covering a range of viscosities, solvent polarities and temperatures are being pursued.

Acknowledgement

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