

Photoinduced charge separation and recombination under distance, orientation, and spin controlled conditions

Jan W. Verhoeven¹ and Michael N. Paddon-Row²

¹Laboratory of Organic Chemistry, IMC, University of Amsterdam, Nieuwe Achtergracht 129,
1018 WS Amsterdam, The Netherlands

²School of Chemistry, University of New South Wales, Sydney 2052, Australia

ABSTRACT. Great efforts have been made to mimic the efficient photoinduced charge separation and concomitant energy storage of natural photosynthetic systems via artificial (supra)molecular constructs as well as to design molecules with potential use for application in molecular electronic circuits. Close packing of such molecules introduces the problem of short-circuiting and cross talk between the separate molecular components. In the present paper the limits will be investigated to which such short-circuiting can be prevented by the use of saturated hydrocarbon (alkane) type insulating structures. Furthermore, as will be shown, several typically molecular scale operating principles such as orbital symmetry and spin multiplicity control can allow the realisation of systems in which fast and efficient charge separation is combined with very slow charge recombination even when the distance between the D(onor) and A(cceptor) moieties is very small.

1. INTRODUCTION

Much interest exists in the study of molecules in which electron transport over relatively large distances can occur under the influence of an external stimulus. This interest is on the one hand triggered by the relation with electron transfer in natural systems [1, 2] including photosynthesis but more recently also by the possibility [3] to bring such molecules in galvanic contact with the “outer world” allowing them to be tested with regard to properties indicated by mind boggling terms like “molecular wires,” “molecular diodes,” “molecular switches,” etc. In the latter cases one mainly concentrates on highly unsaturated and conjugated molecules because the delocalisability of the extended pi-systems they contain in principle warrants a rather easy electron transport. A remarkable example of such work is e.g. constituted by the investigations of Dekker c.s. [4] on the conductivity of single carbon nanotubes. At the other extreme of a molecular conductivity scale one expects to find fully saturated hydrocarbons that also macroscopically (e.g. in the form of paraffin and polyethylene) constitute very effective insulators. However, one has to be careful in extrapolation of macroscopic properties to molecular ones because the distances within molecules are small enough to make that the wave character of electrons comes into full play.

As part of a long standing collaborative program we have extensively investigated the consequences of this wave character, and the ensuing electron transfer by tunneling, in molecular systems that are build up from an electron donor (D) and acceptor (A) connected by

a geometrically well defined alkane “bridge” the latter being varied in length and shape [5–8]. These D-bridge-A molecules were designed in such a way that electron transfer from D to A becomes energetically feasible only after D has been brought in its first singlet excited state by excitation with light ($D + h\nu \rightarrow D^*$). From that excited state, which is about 3.8 eV above the ground state, there is, depending on the length of the bridge and especially on the polarity of the solvent used, a driving force equivalent to a potential difference between 0.1 and 1.0 Volts to transfer one electron from D to A, resulting in charge separation (k_{cs}) and from thereon charge recombination (k_{cr}) to restore the initial state occurs with a driving force in the range of 2.8 to 3.7 Volts [8]. Thus, after excitation with light, two sequential electron transfer processes can be studied within these molecules (see Figure 1).

2. RESULTS AND DISCUSSION

2.1. Tunneling and electron transfer theory.

Electron transfer across the alkane bridges in our D-bridge-A molecules must occur via quantum mechanical tunneling because the electron affinity of the alkane bridge is so low that it is impossible to localise an electron in/on that bridge. Already the basic WKB model [9] for tunneling (see Figure 2) predicts that the rate of electron transfer should decrease exponentially with the length of the bridge (which is equivalent to the barrier width, w , in Figure 2).

However, the situation in molecular systems is more complex than in the WKB model, which describes tun-

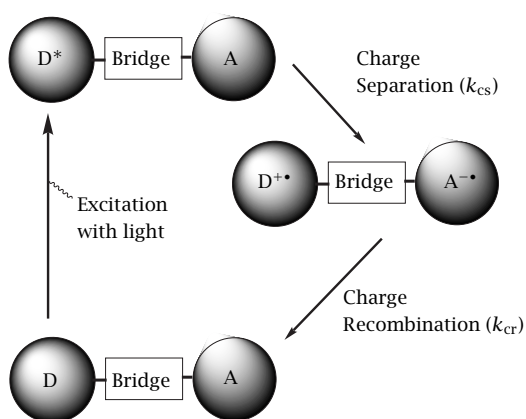


Figure 1. Schematic energy diagram of the consecutive excitation, charge separation and charge recombination events in the D-bridge-A systems under study.

neling between two continuum states across a stationary barrier. In that situation the tunneling particle can always retain the same energy while crossing the barrier. In a molecular system, however, the tunneling occurs between two bound states each characterised by discrete energy levels that in general do not match between both sides of the barrier [10–14]. Efficient electron tunneling then requires that nuclear reorganisation of the system as a whole (i.e. including the eventual surrounding medium) occurs until “resonant conditions” characterised by a symmetrical (electron) potential are established (see Figure 3).

As a result the rate of electron transfer is not only influenced by the height and width of the barrier (that

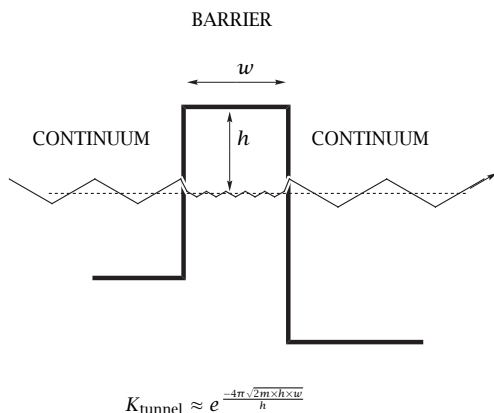


Figure 2. Original Wentzel, Kramers, Brillouin description for tunneling of a particle with mass m between two continua across a stationary barrier with height h and width w .

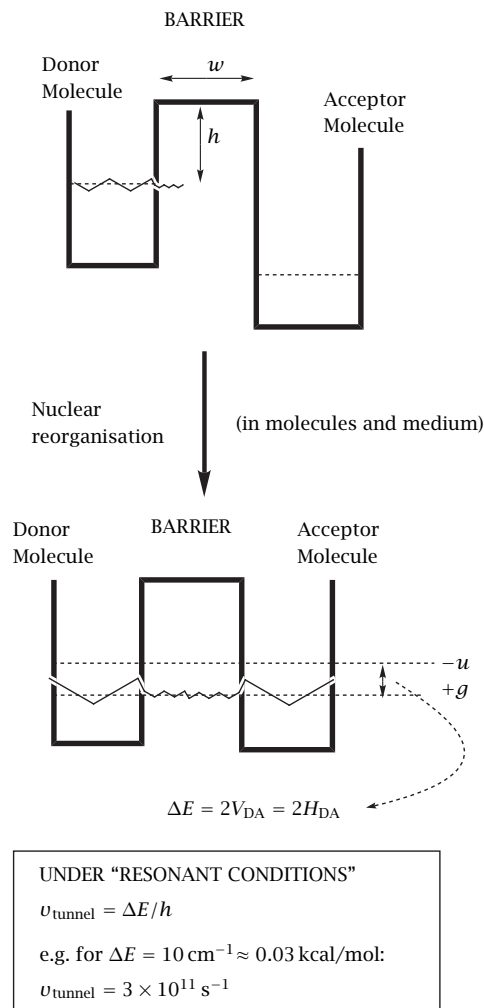


Figure 3. Schematic diagram indicating the effect of nuclear reorganisation in establishing “resonant conditions” for electron tunneling.

govern the resonant level splitting indicated in Figure 3 by $\Delta E = 2V_{DA}$, where V_{DA} is often called the “electronic coupling”) but also by the energy required to induce the nuclear reorganisation that establishes resonant conditions. This consideration is inherent in the well known Marcus theory of electron transfer [15, 16] that expresses the reorganisational Gibbs energy of activation (ΔG^\ddagger) in terms of the overall driving force ($-\Delta G$) and the total reorganisation energy (λ) assuming harmonic potentials for the nuclear motions involved leading to:

$$\Delta G^\ddagger = \frac{(\Delta G + \lambda)^2}{4\lambda}. \quad (1)$$

2.2. Distance dependence of electron transfer across extended alkane bridges. As discussed briefly in the preceding section, the rate of electron

transfer in D-bridge-A molecules depends both on the electronic coupling V_{DA} and upon the Gibbs energy of activation (ΔG^\ddagger) involved in establishing resonant electron tunneling conditions. In a large series of D-bridge-A systems that we have studied [8], the D and A units were designed in such a way [17] as to minimize the influence of ΔG^\ddagger (i.e. $\Delta G^\ddagger \approx 0$) on the photoinduced charge separation. The rates of photoinduced charge separation therefore should mainly or exclusively reflect how the electronic coupling V_{DA} is influenced by the changes in the structure of the alkane bridge.

It should be noted that the condition $\Delta G^\ddagger \approx 0$ is not met for the subsequent charge recombination process and this is the main reason that in some cases charge recombination occurs up to three orders of magnitude slower than charge separation! The first thing we started testing [5, 8, 18] then was the influence of the bridge length on the rate of charge separation using a series of structurally similar, rigidly extended alkane bridges with lengths ranging from a few Å up to about 20 Å. As predicted by basic electron tunneling theory (see above) an exponential distance dependence was observed, that after the latest additions [19] seems to be quite well represented by equation (2), in which the damping factor, β , was found to be as low as 0.8 to 0.7 per Å.

$$k_{cs} \text{ (in sec}^{-1}\text{)} = 10^{14} \exp(-\beta R). \quad (2)$$

This implies that even across a strongly insulating bridge consisting of fully saturated hydrocarbon units electron transfer can readily occur under conditions that minimize the reorganisational activation energy required to achieve a resonant tunneling situation.

2.3. The influence of bridge bending. In the preceding section it was noted that across linear saturated alkane bridges with an extended structure fast long range electron transfer can be achieved with a typical exponential damping factor as low as 0.7–0.8 per Å. This is a very convincing example of how the wave character of electrons allows them to pass via tunneling between regions of space separated by very high energy barriers that would classically be expected to act as total insulators. As schematised by the wavy lines in Figures 2 and 3, such tunneling implies that the wavefunction describing the electron has a very minor but non-zero amplitude inside the barrier region. In other words, in our D-bridge-A molecules the electron transferred is almost completely localised on either D or A but the molecular orbital in which it resides still extends a minor “tail” into the bridge region by mixing between the D or A pi-orbitals and one or more bridge sigma orbitals of the proper symmetry and energy. Such a mechanism is generally referred to as through (sigma) bond interaction (TBI) [20]. It has also been shown via e.g. quantum-chemical calculations

that TBI should be stronger via extended all-s-trans arrays of sigma-bonds than via arrays containing one or more gauche or eclipsed units leading to a more bent or kinked overall bridge configuration.

While we have provided several examples supporting this prediction earlier [21–24], we have recently been able to demonstrate it in a really dramatic fashion and at the same time revealed an additional effect by comparing the rates of photoinduced charge separation in a series (see Figure 4) of three D-bridge-A systems in which the overall length of the bridge was kept constant but its configuration was changed from fully extended (D/A distance 13.4 Å) to partly bent (D/A distance 9.54 Å) and to strongly bent (D/A distance 7.5 Å) [25].

Equation (2), that was derived employing a series of linearly extended bridges, leads to the prediction that the moderate bending from 13.4 Å to 9.54 Å should increase the rate of electron transfer twentyfold. Instead a *ca.* tenfold rate reduction was observed, thus dramatically demonstrating the lower TBI ability of the bent bridge and also indicating that on a molecular scale tunneling theories which only describe a barrier in terms of its width and height are inadequate.

Interestingly, further bending of the bridge to reduce the D/A distance to 7.5 Å does lead to a significant rate enhancement, although still less than the hundredfold

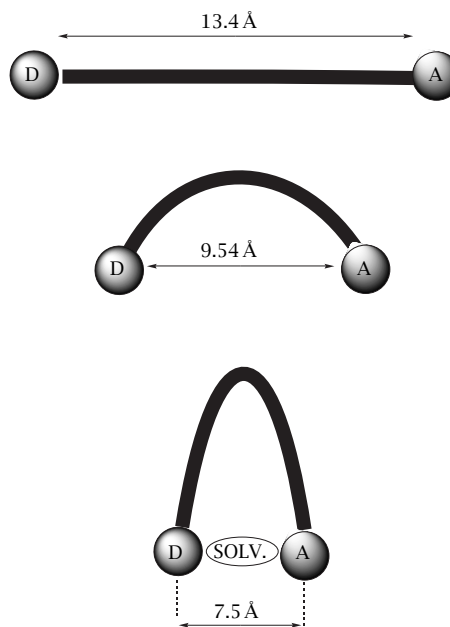


Figure 4. Schematic representation of a series of three D-bridge-A systems with constant bridge length (i.e. 10 sigma bonds) but increasing bridge curvature studied recently to investigate the effect of such curvature on rates of intramolecular electron transfer.

increase predicted by equation (2). At the same time it was found that in this strongly bent system the rate is quite sensitive for the nature of the solvent employed. The latter we propose [25] to be caused by the fact that at 7.5 Å a single solvent molecule fits snugly in the cleft between D and A, thereby allowing through-solvent interaction to add to the overall electronic coupling between D and A.

2.4. Can alkane insulators protect molecular electronics from short circuiting? Our investigations on electron tunneling via saturated hydrocarbon bridges briefly discussed above as well as related investigations by others [26] have indicated that in general the electronic coupling via such saturated hydrocarbon systems and thereby the rate of electron transfer across regions occupied by saturated alkane structures follows an exponential distance dependence, but that the damping factor β (see equation (2)) varies as a function of the nature and configuration of the covalent coupling paths provided by the sigma-bonds that constitute this alkane medium. From the various structures investigated by now it appears that a variation from $\beta = 0.7$ per Å for alkanes optimally structured for through-bond interaction along extended all-trans pathways to $\beta = 1.1$ per Å for those allowing only highly kinked coupling pathways encompasses the whole range of alkane “conductivity”.

It should be noted that even at the upper limit of $\beta = 1.1$ per Å this implies that alkanes allow amazingly fast electron transfer across distances on a molecular scale.

This is demonstrated in Figure 5, where the predicted (see equation (2)) tunneling time ($\tau = 1/k$) has been plotted on a logarithmic scale for various values of β and across distances up to 50 Å. Clearly, even for the best insulator of an alkane type these tunneling times are less than a few minutes for an insulator thickness of 40 Å (4 nm) or less. This seems to imply that although molecular scale components may become available that can act as parts of electronic circuitry, the packing density in such circuitry will have to be limited to distances way beyond 50 Å. In this connection it is important to note that in fact serious insulation problems may arise much earlier in attempts to down scale from the presently achievable *ca.* 100 nm packing distances. This is because already at 100 nm the combination of miniaturisation of distances with the increase of switching frequencies has been found to lead to serious cross-talk of a capacitive and inductive nature. Interestingly, low dielectric constant hydrocarbon insulation instead of the common silicon dioxide insulation is recently being applied to suppress such cross talk.

2.5. Slowing down electron transfer by orbital symmetry control. As evident from what has been discussed above even the high insulating capacity of

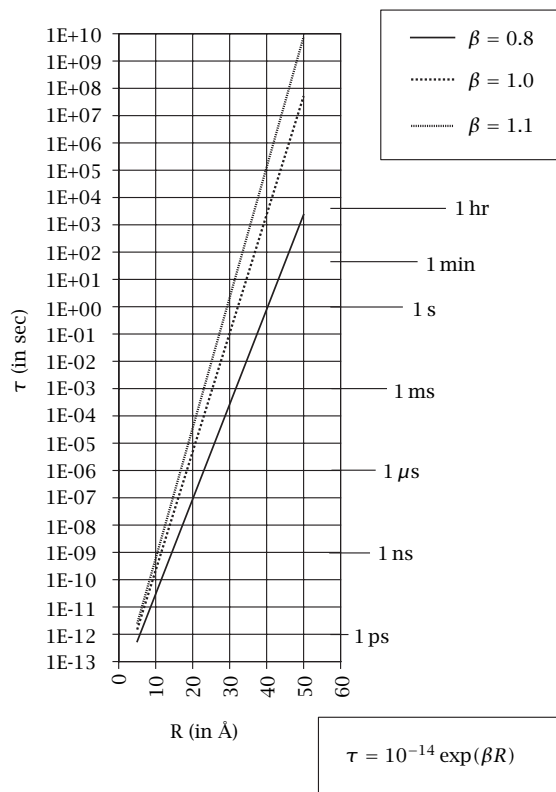


Figure 5. Electron tunneling time predicted by equation (2) for values of the damping factor ranging from $\beta = 0.8$ to 1.1.

alkanes cannot prevent electron tunneling over molecular distances. Nevertheless, inhibition of electron transfer and in particular slowing down charge recombination is highly desirable in many applications. This not only includes the insulation problem in densely packed (molecular) electronic devices, but more in particular also nearly every application in which it is attempted to store light energy by conversion into an electrical (or electrochemical) potential. In the latter field the general trend is to borrow from nature by building complex molecular systems similar to those found in natural photosynthetic units. In these systems an initial photoinduced charge separation step across a relatively small distance is followed by a sequence of thermally driven charge transfer steps that increase the charge separation distance enough to make recombination of the ultimately created hole/electron pair slow because of the very small electronic coupling across the large distance attained. Such schemes not only call for large synthetic efforts, but also unavoidably imply that much of the initial photon energy is wasted in the sequence of down-hill charge separation processes. In principle, molecular symmetry constraints in “simple” D-bridge-A systems provide another possibility to

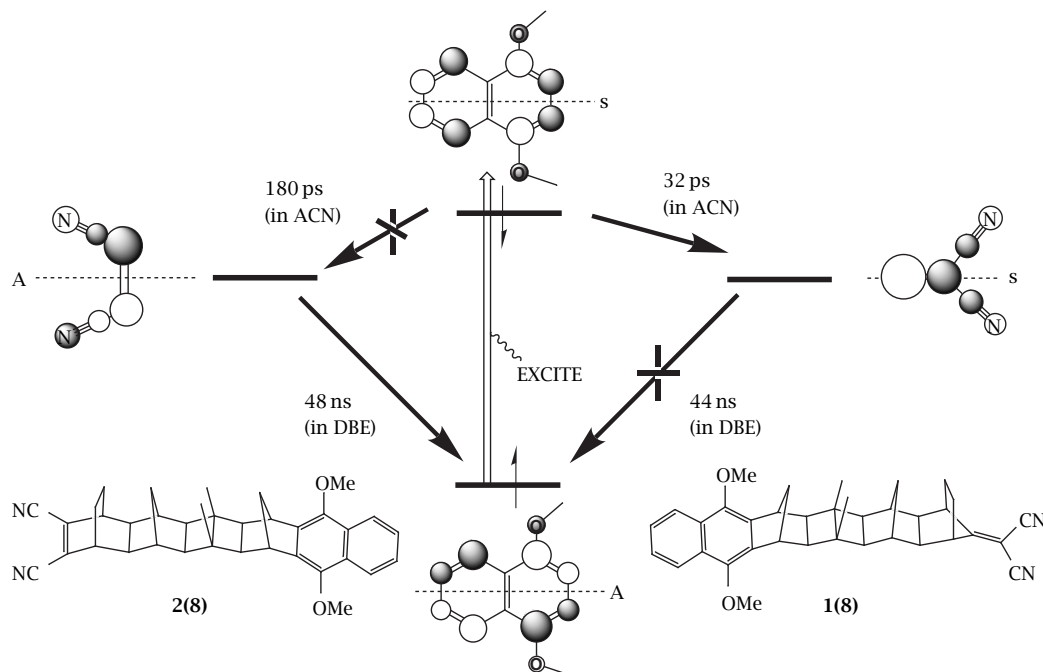


Figure 6. Two rigid D-bridge-A systems with opposite orbital symmetry constraints for the charge separation and charge recombination processes together with the electron transfer time constants actually observed. Symmetry labels *S* and *A* refer to the C_s molecular symmetry. Charge separation times measured in di-*n*-butylether (DBE), charge recombination in acetonitrile (ACN).

combine fast and efficient charge separation with slow charge recombination. This would require the design of conformationally rigid systems in which photoinduced charge separation is symmetry “allowed,” while at the same time charge recombination to the electronic ground-state is symmetry “forbidden”. Several such systems have in fact been designed and tested especially by us [27–29] and by Zimmt *et al.* [30]. Figure 6 shows two such systems studied by us together with the shape of the appropriate frontier molecular orbitals involved in the charge separation and recombination processes. In both systems the electron donor 1,4-dimethoxynaphthalene unit is separated from an electronegatively substituted ethylene electron acceptor by a rigidly extended bridge with an effective length of 8 sigma-bonds in such a way that an overall C_s molecular symmetry is retained. Under these symmetry conditions, and if one would simply assume that the first excited state of the donor can be adequately described by a one electron HOMO to LUMO excited configuration, the photoinduced charge separation in **1(8)** is in principle symmetry “allowed,” while that in **2(8)** is symmetry “forbidden”. Indeed a significant, although certainly not dramatic, increase in the charge separation time (from 32 ps to 180 ps both in acetonitrile) was observed [27]. Regrettably, the charge recombination times of these two systems are, however, nearly equal [27, 28] and

it even appears that charge recombination is slightly faster under the symmetry forbidden conditions pertaining in **1(8)** than under the symmetry allowed conditions in **2(8)**!

The failure to control electron transfer rates via symmetry effects becomes even more evident if we take into account that the symmetry properties of the lowest singlet excited state of the naphthalene donor are probably opposite to that suggested by the oversimplified HOMO to LUMO single electron configuration scheme drawn in Figure 6 [27, 31] so that even the small difference in charge separation times cannot be attributed to symmetry effects. We note that the major reason for the absence of significant symmetry effects on electron transfer rates may probably be the “nonvertical” nature of these processes. I.e., as already discussed in Section 2.1, electron transfer is in general coupled to significant nuclear distortion (reorganisation) and the vibrational modes involved in this reorganisation may significantly diminish or even fully cancel the symmetry restrictions on the electronic interaction matrix element V_{DA} that one would expect from the kind of (ground-state) equilibrium geometry considerations presented in Figure 6.

In Figure 7 this problem is schematically illustrated by drawing the familiar Marcus type parabolic potential energy diagrams for the electronic states involved

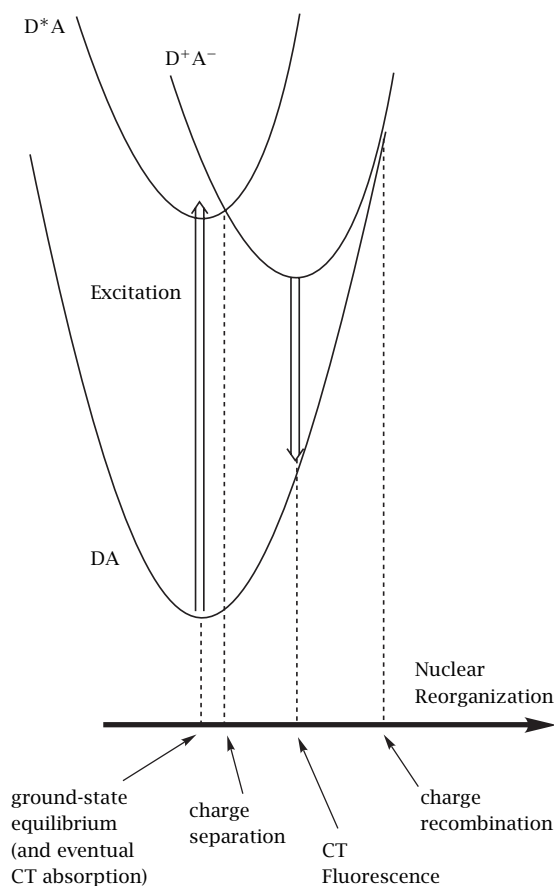


Figure 7. Marcus type energy versus nuclear reorganisation diagram for the excitation, charge separation, charge recombination cycle in D/A systems in which the average nuclear configurations at which radiative or radiationless electron transfer emerges have been marked.

as a function of the nuclear reorganisation pseudo-coordinate. As indicated there, during both radiationless charge separation and charge recombination the nuclear coordinates neither in the reactant state nor in the product state correspond to an equilibrium situation for any of the electronic states. Interestingly, and as also indicated in Figure 7, the eventual radiative electron transfer pathways of charge transfer absorption and charge transfer fluorescence are characterised by a situation in which at least the reactant state has attained an equilibrium geometry. In fact both for charge-transfer absorption and for charge transfer fluorescence very significant symmetry effects on the transition probability have been detected. With respect to charge transfer absorption this refers for instance to a number of electron donor/acceptor cyclophanes one of us reported earlier [32], but in the compounds depicted in Figure 6 this absorption is too weak to detect un-

der the stronger local donor absorption. However, for both **1**[8] and **2**[8] charge transfer fluorescence could be detected in low polarity solvents and from this it was found [28] that the radiative rate constant in **2**[8] is about ten times that in **1**[8], which is in good correspondence with the symmetry allowed respectively forbidden nature of charge recombination in these systems. It should be noted that these radiative recombination processes constitute only a very minor fraction of the overall charge recombination for which the radiationless pathway is overwhelmingly dominant, and therefore the symmetry effects on the radiative pathway cannot be detected in the overall recombination rate constants, the latter being further complicated by branching [33] to local triplet states. It should also be noted that although the symmetry effects on the radiative electron transfer processes thus appear significant, in contrast to those on the radiationless pathways, they still are not so strong that one might employ such symmetry effects as a very efficient rate control mechanism.

As will be discussed in the next section, the control of the electron spin state appears much more promising in this respect.

2.6. Slowing down electron transfer by electron spin control.

In the preceding sections it has been established that in bichromophoric D-bridge-A systems very fast and efficient photoinduced charge separation can be achieved even across rigidly extended saturated hydrocarbon bridges up to > 20 Å in length. The underlying mechanism of electron transfer in these systems is electron tunneling enabled mainly by through bond electronic interaction between D and A via the intervening sigma bonds of the bridge, while in the case of strongly bent bridges this interaction can be augmented by through solvent interaction. It also became clear that in such bichromophoric D-bridge-A systems fast photoinduced charge separation is inevitably followed by fast energy wasting charge recombination. The main reason that this charge recombination is often slower than the charge separation (see e.g. the numbers in Figure 6) appears to be that the former process often occurs deep into the Marcus “inverted region” where the driving force ($-\Delta G$) significantly exceeds the reorganisation energy (λ) thereby inducing a high reorganisational barrier (see equation (1)). This explanation is supported by the observation that the rate of charge recombination increases dramatically upon increasing the solvent polarity which diminishes the driving force by stabilisation of the charge separated state and increases the total reorganisation energy. Thus for the compounds depicted in Figure 6 transfer from e.g. di-n-butylether to acetonitrile diminishes the lifetime of the charge separated state from > 40 ns to the sub-nanosecond domain. In the preceding section we have also shown that the conceptually elegant application of orbital symmetry restrictions does not provide an

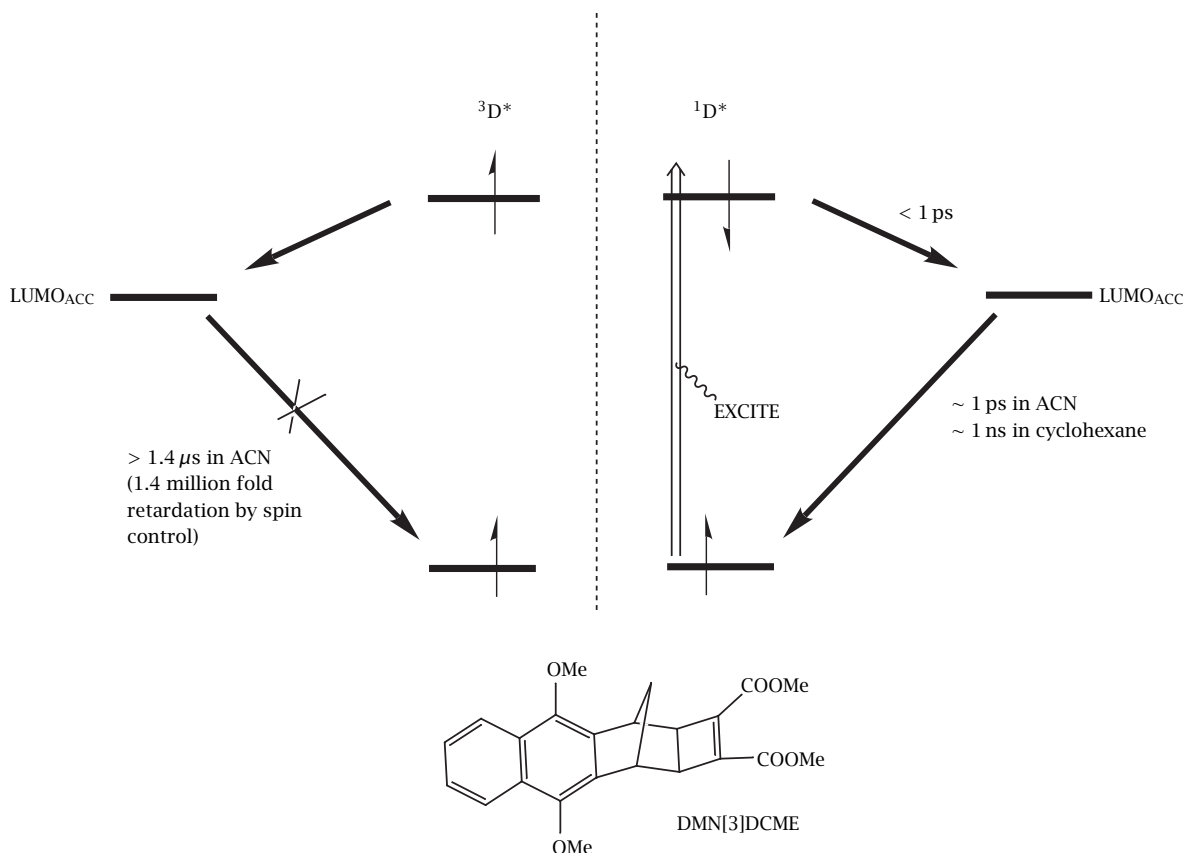


Figure 8. Induction of a charge transfer triplet state in DMN[3]DCME via intermolecular sensitisation with benzophenone in polar solvents allows charge separation in this D-bridge-A system to be maintained on a microsecond timescale whereas charge recombination in the singlet manifold occurs on a picosecond timescale in the same solvent.

efficient method to increase the ratio of charge separation and charge recombination rates even in very rigid D-bridge-A systems. An alternative way to achieve this goal, that has been employed extensively in intermolecular charge transfer systems, is based on the fact that the product of photoinduced charge transfer between closed shell systems always has the character of a radical (ion)pair which can in principle either have an overall singlet or triplet electron spin configuration. While recombination from the singlet configuration to the ground state is spin allowed, that from the triplet is spin forbidden. Many problems arise, however, when one envisages how to create a triplet charge separated state in a rigid D-bridge-A system. Inevitably direct excitation of either D or A leads to a local singlet state from which electron transfer to populate a singlet charge transfer state is bound to occur rapidly. As a result, for rigid D-bridge-A systems only in some isolated cases charge transfer triplet states appear to have been populated by employing a D or especially an A group that undergoes extremely rapid intersystem crossing (isc) in its locally excited state [34, 35]. One might consider the possibility to improve the competition between local

isc and singlet charge transfer by increasing the length of the bridge and thereby exponentially decreasing the rate of charge transfer. However, this also leads to a situation in which the electronic coupling between D and A becomes so small that an eventually formed triplet charge transfer state is nearly degenerate with the corresponding singlet state thus allowing rapid hyperfine interaction driven interconversion between singlet and triplet thereby essentially nullifying their lifetime difference [36]. We have recently found a way around these problems employing a scheme [37] in which the local triplet state of one of the chromophores (in this case the donor) is populated without invoking its singlet as an intermediate. This can simply be achieved by excitation of an added external triplet sensitizer of which the singlet energy is below that of both the D and A chromophores, but which has a triplet energy above that of either D or A.

This method was applied [37] to the rigid D-bridge-A system DMN[3]DCME (see Figure 8) with benzophenone as a triplet sensitizer and in acetonitrile as a solvent. In the latter solvent direct excitation of DMN[3]DCME leads to a singlet charge separation

rated state which recombines to the ground-state on a (sub)picosecond time scale. This fast charge recombination is to be expected in view of the strong electronic coupling across the short hydrocarbon bridge and the small reorganisational barrier for charge recombination (as well as separation) prevailing under polar solvent conditions (see above). Application of equation (2) with $R \approx 4 \text{ \AA}$ leads to an estimated shortest electron transfer time of about 0.25 ps.

Upon sensitisation with benzophenone it was observed by transient absorption spectroscopy that energy transfer from the benzophenone triplet to the DMN donor chromophore occurs [33] followed by triplet state charge separation [37]. The intramolecular triplet charge transfer state was found to recombine very slowly giving it a lifetime of about 1.4 microseconds, i.e. more than a millionfold of that of the corresponding singlet charge transfer state. Whether this slow recombination directly produces the electronic ground state or involves (uphill) intersystem crossing to the singlet charge transfer state that next recombines very rapidly to the ground state cannot be decided at the moment.

3. CONCLUSIONS

The construction of conformationally rigid D-bridge-A systems containing a saturated alkane type bridge and their photophysical investigation have allowed us to reveal the degree to which (photoinduced) electron transfer can be mediated via such alkane bridges in competition with mediation via the surrounding medium. The structure and especially the configuration of the alkane bridge significantly modify the degree to which it is able to mediate "through-bond" electronic interaction. However, even alkane bridges that deviate strongly from the optimal configuration for through-bond interaction can be predicted to mediate electron transfer over remarkably large distances. Thus, at molecular scale distances even saturated alkanes appear to be rather poor insulators, which may set an ultimate limit to the packing density achievable in (molecular) electronic circuits.

While molecular (orbital) symmetry constraints might in principle allow the selective inhibition of electron transfer in rigid molecular systems, it appears that at ambient temperature such symmetry restrictions can provide only minor kinetic effects due to vibrational coupling effects. Quite effective inhibition of electron transfer over short distances is, however, possible by control of the relative spin state of the excited charge transfer state of a D-bridge-A molecule and the ground state. The efficiency of the latter approach, however, requires many conditions to be met simultaneously such as the availability of an effective way to enter the charge transfer triplet state (e.g. by sensitised excitation), a

large exchange interaction between the radical sites on D and A in that state (to avoid rapid hyperfine interaction mediated intersystem crossing between triplet and singlet), and the absence of local triplet states with an energy below that of the charge-transfer triplet. That these requirements can be met simultaneously has been demonstrated convincingly via the study of the rigid and compact DMN[3]DCME system.

References

- [1] J. R. Winkler and H. B. Gray, *J. Biol. Inorg. Chem.* **2** (1997), 399.
- [2] C. C. Page, C. C. Moser, X. Chen, and L. Dutton, *Nature* **402** (1999), 47.
- [3] J. Jortner and M. A. Ratner, *Molecular Electronics*, Blackwell, London, 1997.
- [4] H. W. C. Postma, M. deJonge, Z. Yao, and C. Dekker, *Phys. Rev. B* **62** (2000), 10653.
- [5] N. S. Hush, M. N. Paddon-Row, E. Cotsaris, H. Oevering, J. W. Verhoeven, and M. Heppener, *Chem. Phys. Lett.* **117** (1985), 8.
- [6] J. M. Warman, M. P. d. Haas, H. Oevering, J. W. Verhoeven, M. N. Paddon-Row, A. M. Oliver, and N. S. Hush, *Chem. Phys. Lett.* **128** (1986), 95.
- [7] J. M. Warman, M. P. d. Haas, M. N. Paddon-Row, E. Cotsaris, N. S. Hush, H. Oevering, and J. W. Verhoeven, *Nature* **320** (1986).
- [8] H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven, and N. S. Hush, *J. Am. Chem. Soc.* **109** (1987), 3258.
- [9] J. G. Simmons, *J. Appl. Phys.* **34** (1963), 1793.
- [10] H. H. Limbach and J. Hennig, *J. Chem. Phys.* **71** (1979), 3120.
- [11] J. Brickmann, *Ber. Bunsenges. physik. Chem.* **74** (1970), 331.
- [12] M. D. Harmony, *Chem. Soc. Rev.* **1** (1972), 211.
- [13] J. R. de la Vega, *Acc. Chem. Res.* **15** (1982), 185.
- [14] R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.* **36** (1962), 1980.
- [15] R. A. Marcus, *J. Chem. Phys.* **43** (1965), 679.
- [16] N. Sutin, *Acc. Chem. Res.* **15** (1982), 275.
- [17] J. Kroon, J. W. Verhoeven, M. N. Paddon-Row, and A. M. Oliver, *Angew. Chem. Int. Ed. Engl.* **30** (1991), 1358.
- [18] J. W. Verhoeven, J. Kroon, M. N. Paddon-Row, and A. M. Oliver, *Photoconversion Processes for Energy and Chemicals*, D. O. Hall and G. Grassi (eds.), Elsevier Science Publ. Co, London, 1989, p. 100.
- [19] M. Seischab, T. Lodenkemper, A. Stockmann, S. Schneider, M. Koeberg, M. R. Roest, J. W. Verhoeven, J. M. Lawson, and M. N. Paddon-Row, *Phys. Chem. Chem. Phys.* **2** (2000), 1889.
- [20] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.* **90** (1968), 1499.
- [21] P. Pasman, J. W. Verhoeven, and T. J. deBoer, *Tetrahedron Lett.* (1977), 207.

- [22] J. Kroon, J. W. Verhoeven, A. M. Oliver, and M. N. Paddon-Row, *Recl. Trav. Chim. Pays-Bas* **107** (1988), 509.
- [23] A. M. Oliver, D. C. Craig, M. N. Paddon-Row, J. Kroon, and J. W. Verhoeven, *Chem. Phys. Lett.* **150** (1988), 366.
- [24] J. M. Lawson, D. C. Craig, M. N. Paddon-Row, J. Kroon, and J. W. Verhoeven, *Chem. Phys. Lett.* **164** (1989), 120.
- [25] N. R. Lokan, M. N. Paddon-Row, M. Koeberg, and J. W. Verhoeven, *J. Am. Chem. Soc.* **122** (2000), 5075.
- [26] J. F. Smalley, S. F. Feldberg, C. E. D. Chidsey, M. R. Linford, M. D. Newton, and Y. Liu, *J. Phys. Chem.* **99** (1995), 13141.
- [27] J. M. Kroon, PhD Thesis, University of Amsterdam, 1992.
- [28] A. M. Oliver, M. N. Paddon-Row, J. Kroon, and J. W. Verhoeven, *Chem. Phys. Lett.* **191** (1992), 371.
- [29] J. W. Verhoeven, J. Kroon, M. N. Paddon-Row, and J. M. Warman, *Supramolecular Chemistry*, V. Balzani and L. DeCola (eds.), NATO ASI Series Vol. **371**, Kluwer Academic Publishers, Dordrecht, 1992, p. 181.
- [30] Y. Zeng, and M. B. Zimmt, *J. Am. Chem. Soc.* **113** (1991), 5107.
- [31] J. R. Reimers, N. S. Hush, D. M. Sammeth, and P. R. Callis, *Chem. Phys. Lett.* **169** (1990), 622.
- [32] L. G. Schroff, A. J. A. vanderWeerd, D. J. H. Staalman, J. W. Verhoeven, and T. J. deBoer, *Tetrahedron Lett.* (1973), 1649.
- [33] M. R. Roest, A. M. Oliver, M. N. Paddon-Row, and J. W. Verhoeven, *J. Phys. Chem.* **101** (1997), 4867.
- [34] D. Anglos, V. Bindra, and A. Kuki, *J. Chem. Soc. Chem. Commun.* **2** (1994), 213.
- [35] S. I. vanDijk, C. P. Groen, F. Hartl, A. M. Brouwer, and J. W. Verhoeven, *J. Am. Chem. Soc.* **118** (1996), 8425.
- [36] M. Wegner, H. Fischer, M. Koeberg, J. W. Verhoeven, A. M. Oliver, and M. N. Paddon-Row, *Chem. Phys.* **242** (1999), 227.
- [37] L. Hviid, A. M. Brouwer, M. N. Paddon-Row, and J. W. Verhoeven, *Chem. Phys. Chem.* (2001), 232.

