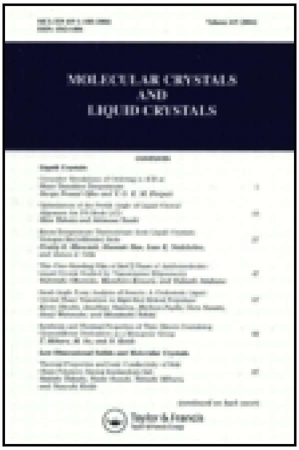

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Opto-Electric Molecules Studied by Time-Resolved Microwave Conductivity (Trmc)

John M. Warman [a] , Stephan A. Jonker [a] , Matthijs P. De Haas [a] , Jan W. Verhoeven [b] & Michael N. Paddon-row [c]

[a] IRI, Delft University of Technology, Mekelweg 15, 2629 JB, DELFT, The Netherlands

[b] Organic Chemistry Department, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS, AMSTERDAM, The Netherlands

[c] School of Chemistry, University of New South Wales, PO Box 1, Kensington, NSW, 2033, Australia

Version of record first published: 04 Oct 2006.

To cite this article: John M. Warman , Stephan A. Jonker , Matthijs P. De Haas , Jan W. Verhoeven & Michael N. Paddon-row (1993): Opto-Electric Molecules Studied by Time-Resolved Microwave Conductivity (Trmc), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 234:1, 121-126

To link to this article: http://dx.doi.org/10.1080/10587259308042906

Mol. Cryst. Liq. Cryst. 1993, Vol. 234, pp. 121–126
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

OPTO-ELECTRIC MOLECULES STUDIED BY TIME-RESOLVED MICROWAVE CONDUCTIVITY (TRMC)

JOHN M. WARMAN*, STEPHAN A. JONKER*, MATTHIJS P. DE HAAS*,
JAN W. VERHOEVEN** AND MICHAEL N. PADDON-ROW†.

*IRI, Delft University of Technology, Mekelweg 15, 2629 JB DELFT, The Netherlands. **Organic Chemistry Department, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS AMSTERDAM, The Netherlands. †School of Chemistry, University of New South Wales, PO Box 1, Kensington, NSW, 2033 Australia.

Abstract Charge separation in the singlet and triplet excited states of donor-spacer-acceptor, DSA, molecules can be studied using the flash-photolysis time-resolved microwave conductivity (TRMC) technique. Highly dipolar, D^+SA^- states with microsecond lifetimes can result from intersystem crossing and through-bond coupling for π-bond conjugated and sigma-bond separated donor-acceptor compounds respectively.

INTRODUCTION

Proposals for molecular scale optical switching and data storage devices have been mainly based either on photochemical effects such as photobleaching and photo-isomerisation or on low temperature "hole burning" in environmentally broadened absorption spectra. Less attention has been paid to the possibility of using opto-electric effects in which photon absorption results in intramolecular charge separation. An obvious barrier to the implementation of such effects in practical switching devices is the limited lifetime of the charge transfer (CT) state which is usually only a few nanoseconds or less. Extension of the lifetime of CT states into the microsecond region could possibly lead to applications in systems for which either long-term memory is unnecessary or memory refreshment is possible.

A major aim of our recent research programme has been to gain insight into the mechanisms controlling photon-induced intramolecular charge transfer and the influences of molecular structure and molecular environment on the efficiency and dynamics of charge separation. In the present report we illustrate how the quantum mechanical effects of intersystem crossing and electron tunnelling can extend the lifetime of highly dipolar, CT states to at least microseconds.

TECHNIQUE

The main experimental tool used in these investigations is the flash-photolysis time-resolved microwave conductivity (TRMC) technique. Using

TRMC we can monitor, with nanosecond time resolution, changes in the microwave conductivity, $\Delta\sigma(\omega) = \Delta\epsilon''/\omega\epsilon_0$, of a dilute solution of a photoreceptor molecule which result from an increase in dipole moment on photo-excitation. $\Delta\sigma(\omega)$ is related to the concentration, N_*, dipole moment, μ_*, and dipole relaxation time, τ_D, by

$$\Delta\sigma(\omega) = (\epsilon' + 2)^2(\mu_*^2 - \mu_0^2)F(\omega\tau_D)N_*/27k_BT\tau_D \qquad (1)$$

ϵ' and ϵ'' are the relative permittivity and dielectric loss of the solution, ϵ_0 is the permittivity of vacuum, ω is the radian microwave frequency, μ_0 is the ground state dipole moment, k_BT is the characteristic thermal energy and $F(\omega\tau_D)$ is the Debye dispersion term.

The temporal form of $\Delta\sigma(\omega)$ provides information on the kinetics of formation and decay of the (transient) photo-product. The absolute magnitude of $\Delta\sigma(\omega)$ provides quantitative information on the degree of photo-induced intramolecular charge separation.

The microwave circuitry, its operation and the method of data assimilation and reduction have been fully described elswhere[1]. Details of importance other than those given in figure 1 are that the laser intensity at the sample is *ca* 10 mJ/cm^2, the optical density of the solutions are usually close to 1 (1 cm path length) and the number of photons absorbed per solute molecule in the irradiated region is usually much less than 1. The overall response time is *ca* 5 ns.

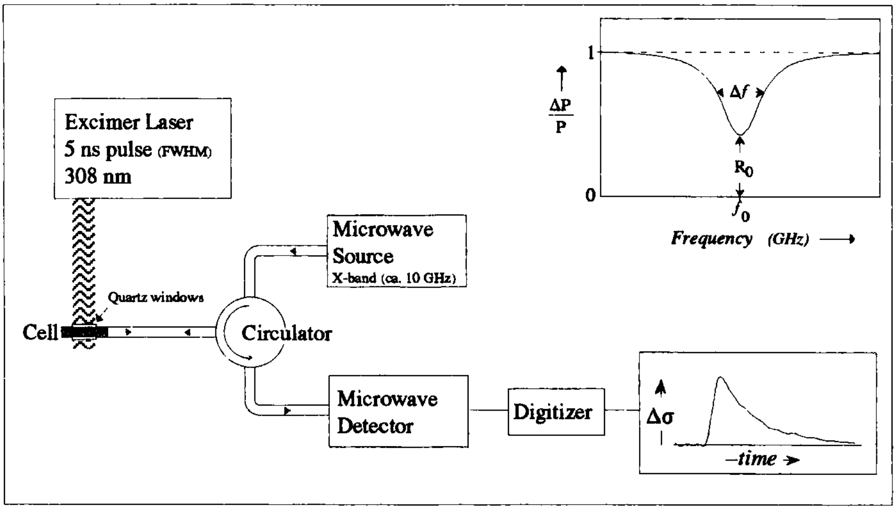

FIGURE 1 A schematic diagram of the TRMC apparatus.

RESULTS AND DISCUSSION

The vast majority of molecules which exhibit opto-electric behaviour consist of a donor moiety, D, and an acceptor moiety, A, separated by an organic spacer, S. The spacer can be either a conjugated system of π-bonds as in "classical" donor-acceptor compounds, or it can consist of a linear array of σ-bonds. In the former case the coupling between D and A is large enough that photoexcitation can result in a direct, Franck-Condon transition to a highly dipolar CT state. In the second case the D-A coupling is extremely weak and a vertical transition usually leads initially to local excitation of the donor or acceptor chromophore. In both cases excitation occurs within the singlet manifold and deactivation via fluorescent and/or radiationless processes will usually occur within a few nanoseconds.

Two processes can occur however which can result in the formation of a $D^{+}SA^{-}$ state which is metastable with respect to the ground state resulting in a substantial increase in the duration of charge separation. Both processes are based on the quantum mechanical properties of the electron: spin-inversion, or intersystem crossing, in the case of DSA compounds with conjugated spacers and through-bond electron tunnelling in the case of sigma-bonded spacers.

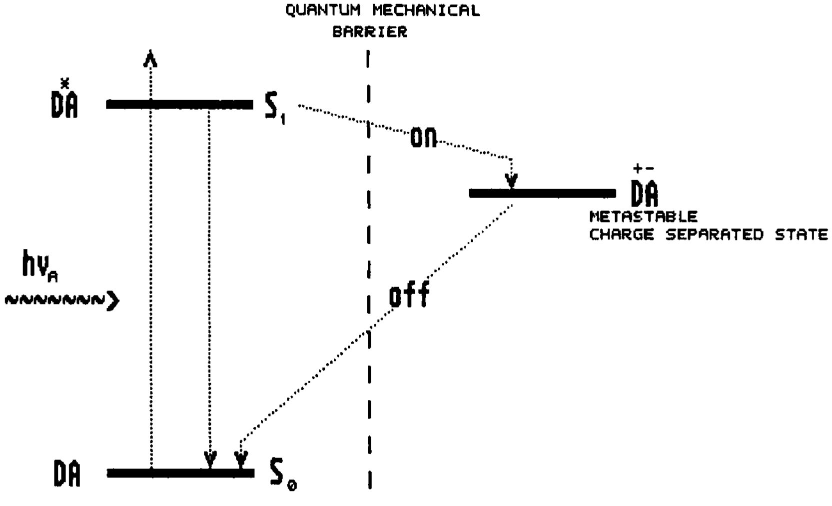

FIGURE 2 A schematic representation of a 3-state molecular opto-electric switch in which a quantum mechanical barrier exists between the relaxed S_1 state and a metastable charge separated state.

Intersystem crossing in conjugated DSA compounds

Interconversion between singlet and triplet spin states of a molecule are in zero order strictly forbidden by the conservation of momentum rule. When coupling between the spin of an electron and the orbital motion of other electrons in the molecule is "allowed" conservation of momentum can be achieved by spin-orbit momentum exchange and S --> T transitions become possible. The change in orbital momentum required results in $^1n\pi^*$ --> $^3\pi\pi^*$ transitions being less strictly forbidden than $^1\pi\pi^*$ --> $^3\pi\pi^*$. If the energy conditions are favourable in the former case, i.e. the energy differential is small, very rapid intersystem crossing can in fact occur and favourably compete with decay processes via the singlet manifold. This is the case particularly for certain aromatic compounds and compounds containing the C=O group. The rate of intersystem crossing is expected to decrease markedly with increasing energy differential (positive or negative) between the relaxed singlet state and the triplet state to which transfer occurs. Factors which change the relative positions of the levels only slightly can therefore result in dramatic changes in the rate of intersystem crossing and large differences even between compounds which are structurally and chemically very similar.

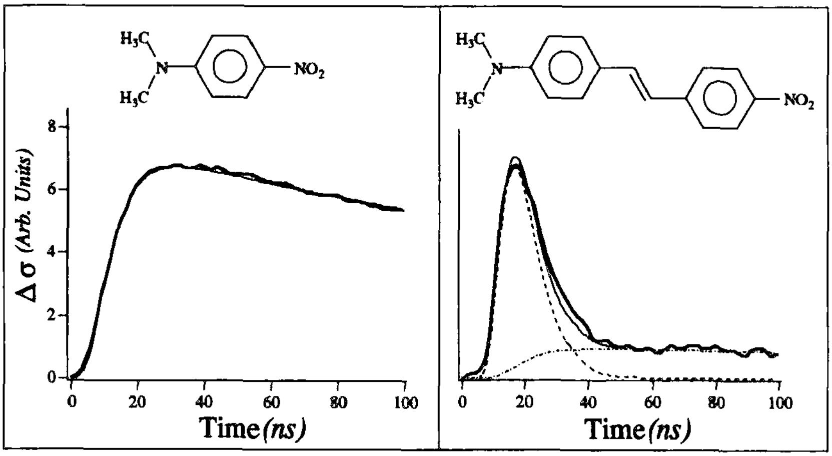

FIGURE 3 TRMC traces found on flash photolysis of benzene solutions of the solutes shown. On the left, due to very rapid intersystem crossing, only a long-lived dipolar transient (> 1μs) attributable to the triplet state is observed. On the right the major, short-lived contribution is from the singlet state (lifetime 3 ns), and only a small triplet state contribution ($\phi_{isc} \approx 0.05$) is apparent. The dashed lines are the calculated singlet and triplet contributions to the signal.

In figure 3 are shown TRMC transients for p-N,N-dimethylamino-nitrobenzene (DMANB) and p,p'-N,N-dimethylamino-nitrostilbene (DMANS). In both cases the large transient conductivity changes indicate the formation of highly dipolar excited states. In the case of DMANB the singlet state is very short-lived (subnanosecond) mainly due to rapid intersystem crossing. In this case therefore the transient is ascribable completely to the highly dipolar triplet state which has a lifetime in excess of a microsecond. In the case of DMANS the S_1 state has a much longer lifetime of *ca* 3 ns and this dominates the TRMC transient as a short-lived component. A long-lived dipolar triplet state is still produced but with a quantum yield of only approximately 5% compared with the larger than 50% for DMANB.

The results in figure 3 serve as a general illustration of both the formation of highly dipolar, long-lived triplet states on photolysis of conjugated DSA compounds and in addition the sensitivity of the intersystem crossing process to changes in the spacer unit. A continuous decrease in triplet yield with increasing length of the conjugated spacer has been found. The sensitivity extends also to changes in the substituents on the amino nitrogen with much larger triplet yields in general being found for the amino group itself and a continual decrease with increasing alkyl substitution[2].

Because of the highly dipolar nature of the excited singlet and triplet states, the relative positions of the S_1 and triplet state levels and hence the intersystem crossing efficiency would be expected to be extremely sensitive to the solvent as is found. In the case of DMANS for example the yield of triplet state is found to decrease from *ca* 50% for saturated hydrocarbons to 5% for benzene and only 2% for para-dioxane, i.e. in order of increasing effective solvent polarity[1].

Changing the donor and acceptor groups from for example amino to hydroxy or from nitro to cyano or sulphone also changes the photophysics completely as might be expected. We hope eventually to be able to determine at least some of the general underlying rules for triplet state formation for this type of compound. Even if the opto-electric effect shown by these molecules turns out to be of no practical use, their proven potential importance in polymeric, non-linear optical devices makes a better understanding of their photophysics worthwhile.

Through-bond electron transfer in non-conjugated DSA compounds

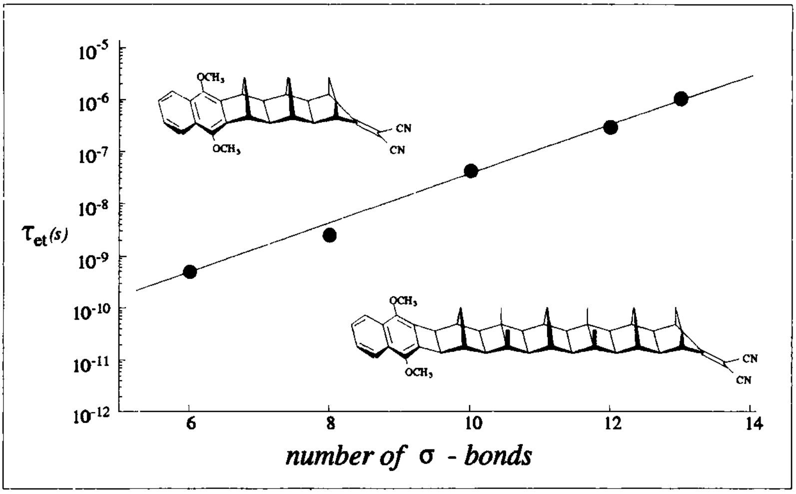

FIGURE 4 The points are the lifetimes of the fully charge separated state of a series of sigma-bond separated DSA compounds plotted as a function of the number of intervening sigma bonds. The molecular structures of the molecules corresponding to the extreme left and right data points are also shown. The data were obtained by TRMC using para-dioxane as solvent.

According to classical organic chemistry the presence of a purely sigma bonded spacer between donor and acceptor should prohibit electron transfer between the two. Recent experimental evidence however has shown that efficient charge separation can occur on photoexcitation even with spacers up to 15 Å long[3,4]. This is attributed to quantum mechanical tunnelling through the hydrocarbon barrier with the necessary wave-function overlap between states being accentuated by virtual electron and hole states within the barrier - an effect now termed "superexchange" or "through-bond coupling"[5,6].

Two molecules of a series[3] that has been used to illustrate the occurrence of this effect are shown in figure 4. They consist of a dimethoxynaphthalene donor entity (the photo-receptor) and a dicyanoethylene acceptor. Donor and acceptor are held rigidly apart by a three-dimensional norbornane type bridge which ensures both longitudinal and rotational integrity of the structure during and after electron transfer. TRMC measurements on these compounds have shown charge separation to be complete resulting in dipole moments up to *ca* 80 Debye[7]. The quantum yield of charge separation in benzene and more polar solvents is found to be close to unity even for a 12 sigma-bond spacer[7].

In figure 4 we show the lifetime of the charge separated state as a function of the length of the spacer for dioxane as solvent. This is seen to increase close to exponentially with distance as would be expected for an electron tunnelling process. For the longest, 13-bond, compound the lifetime of the D^+SA^- state is seen to be slightly longer than a microsecond, i.e. more than 3 orders of magnitude longer than for the 6-bond compound. The rate of the forward charge separation step has been found, using time-resolved fluorescence techniques, to be close to two orders of magnitude faster than recombination in dioxane[2,7].

It is worth pointing out that much longer lifetimes of D^+SA^- states are undoubtedly achievable via intersystem crossing in the conjugated DSA compounds since triplet state lifetimes can extend to as long as seconds in rigid media. Charge separation for the conjugated compounds is however never complete, as it is for the sigma-bond spacers, and dipole moments tend to saturate at *ca* 30 Debye with increasing spacer length[8].

ACKNOWLEDGMENT

The research was supported by the Netherlands Ministry of Economic Affairs Innovation-Oriented Research Programme on Polymer Composites and Special Polymers and by the Australian Research Council, the Netherlands Foundation for Chemical Research (SON) and the Organization for the Advancement of Research (NWO).

REFERENCES

1) M.P. de Haas and J.M. Warman, Chem. Phys., 73, 35 (1982).
2) J.M. Warman, S.A. Jonker, M.P. de Haas, J.W. Verhoeven and M.N. Paddon-Row, SPIE, 1559, 159 (1991).
3) J.M. Warman, K.J. Smit, M.P. de Haas, S.A. Jonker, M.N. Paddon-Row, A.M. Oliver, J. Kroon, H. Oevering and J.W. Verhoeven, J. Phys. Chem., 95, 1979 (1991).
4) M.R. Wasielewski, Photoinduced Electron Transfer, (Elsevier, Amsterdam, 1988) M.A. Fox and M. Chanon eds., part D, p 303.
5) R. Hoffmann, Accounts Chem. Res., 4, 1 (1971).
6) M.D. Newton, Chem. Rev., 91, 767 (1991).
7) M.N. Paddon-Row, A.M. Oliver, J.M. Warman, K.J. Smit, M.P. de Haas, H. Oevering and J.W. Verhoeven, J. Phys. Chem., 92, 6958 (1988).
8) S.A. Jonker, J.M. Warman, M.P. de Haas and M.N. Paddon-Row, Sensors and Actuators (Kluwer, Deventer, 1990) A. Driessen ed, p 315.