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

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Version of record first published: 24 Sep 2006

To cite this article: M. A. Robb, M. J. Bearpark, P. Celani, F. Bernardi & M. Olivucci (2000): Theoretical Modelling as a Possible Tool in the Design of Photochromic Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 344:1, 31-39

To link to this article: http://dx.doi.org/10.1080/10587250008023811

Mol. Cryst. Liq. Cryst., 2000, Vol. 344, pp. 31-39
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Theoretical Modelling as a Possible Tool in the Design of Photochromic Systems

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In photochemical processes, the reactant resides on an excited state potential energy surface and the products accumulate on the ground state. Thus the reaction path must have at least two branches: one located on the excited state and the other located on the ground state energy surface. The novel feature of photochemistry is the "funnel" region where the excited state reactant or intermediate is delivered to the ground state.

A modelling strategy for the complete description of what happens at the molecular level *from energy absorption to product formation,* will be described. The nature of the ground/excited state surface topology that is a requirement for photochromism will be outlinedas well as the current theoretical tools that can be used in modelling. Applications will be briefly reviewed.

HOW DOES POTENTIAL SURFACE TOPOLOGY CONTROL PHOTOCHEMICAL AND PHOTOPHYSICAL PROCESSES?

For the last 10 years we have had an extensive research program focused on attempting to understand the nature of photochemical and photophysical processes at the molecular level. Some of this work is summarized in accessible reviews (see references 1—3). As a result of this work, one not only has some powerful computational tools, but we

hope we have established a conceptual basis for the understanding of photochemical and photophysical processes that can be applied as part of a rational design process for new species. Accordingly, the purpose of this paper is to review some of these ideas and to illustrate their applicability.

Photochromism is the reversible transformation of chemical species between two states whose absorption spectra are recognizably different, brought about in at least one direction by light. It is clear from the preceding statement that photochromism is intrinsically associated with an non-adiabatic process. The reaction coordinate must begin on the excited state reached after photoexcitation and terminate on the ground state following a radiationless or non-adiabatic pathway. The reactant must then be regenerated either via an adiabatic pathway (thermal) on the ground state, or via a non-adiabatic pathway following photoexcitation of the newly generated ground state product.

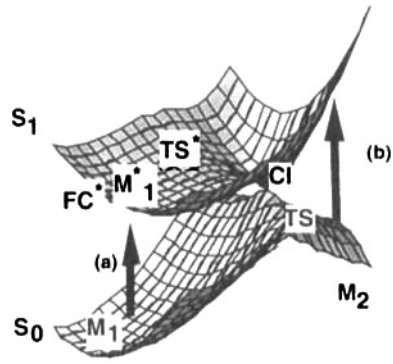


Figure 1. A model potential surface for a photochromic system.

A potential surface model consistent with this concept is shown in figure 1. Photoexcitation (a) generates a system on the S_1 excited surface. The

system may then evolve on S_1 in a manner similar to a thermal reaction path, namely, via a minimum M_1^* and a possible transition state TS*. However, this S_1 reaction path must terminate at a point of crossing called a conical intersection CI (see the general discussion in references 1-3 and more focused discussion in references 4-7). This is the "photochemical funnel" [5,6]where the non-adiabatic event occurs and the reaction path must continue on the ground state. At the CI, the ground state reaction path either evolves toward a new chemical species, M_2, or it evolves back to the reactant M_1. The new chemical species, in turn, can revert to the reactant minimum, M_1, via a thermal process involving a transition state TS, or, following excitation (b),to S_1 again, it can decay via the CI, to the reactant minimum M1 again. Clearly the efficiency of this process must depend both on the topology of S_1 and the nature of the ground state surface in the region of the M_1 minimum. On the one hand, one needs to ensure that the passage through the conical intersection CI is directed towards the desired M_2 minimum and that the passage toward regeneration of the reactant M_1 is less favoured. On the other hand, the ground state minimum M2 must obviously be stable towards further decomposition and have the desired absorption characteristics and barrier with respect to be thermal formation of M_1 from M_2.

The conical intersection shown in figure 1 is a peaked intersection, the crossing point is that a "local minimum". Shown in figure 2 is a different conical intersection topology. This conical intersection is "sloped" in the sense that the surface crossing occurs at an energy that lies higher than the minimum. In this case the generation of a new chemical species, cannot occur and the process following photoexcitation (a) can only yield the starting reactant.

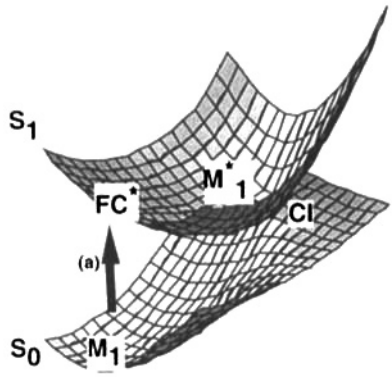


Figure 2. A model potential surface for an "aborted" photochemical process

Thus it is clear from the "cartoons" shown in figures 1 and 2 that the nature of the reaction path on the excited state and the conical intersection surface topology are crucial features in the design of photochromic systems. The flux of the motion along S_1 needs to be strongly directed toward the S_0 product minimum M_2 in figure 1. Thus the occurrence of the appropriate transition state TS* must be such that it forms a bottleneck which directs this flux accordingly and avoids the alternate decay path from the conical intersection that would regenerate the reactant species M_1. Further, a surface crossing of the form shown in figure 2, must not occur in the photochemical system, since the process passing through this CI can only generate the photophysical event corresponding to the regeneration of the reactant M_1 species.

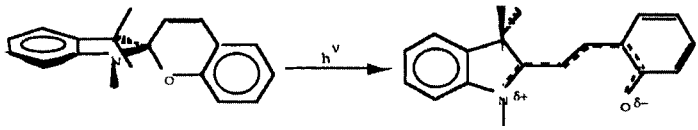
MODELLING PHOTOCHEMICAL AND PHOTOPHYSICAL PROCESSES

The tools for modelling photochemical processes have been developed over the last 10 years and are now available in many standard quantum chemistry packages. Space limitations in this paper preclude a detailed discussion and we refer the reader to our recent review [3] for a full survey. Accordingly we will limit our discussion to brief mention of those methods that we have developed and which are distributed as part of standard software such as the Gaussian package[8]. Since one needs a balanced representation of ground and excited states, standard methods such as SCF and DFT are not applicable. Methods such as CASSCF [9] and multi-reference perturbation methods [10,11] (CAS-MP2 or CASPT2) are essential. Using these methods, the excited and ground state reaction paths can be mapped out in the standard way. The new tools required for investigation of photochemical reaction paths relate to a) characterizing the conical intersection[12], b) finding reaction paths from the FC point or from the CI point, where the gradient of the potential surface is not zero, and c) dynamics studies that follow the evolution of the system according to Newtonian dynamics using the gradient of the electronic wavefunction computed using the methods of quantum chemistry (see for example ref. 14-16)

SOME CASE STUDIES

Photochromic reactions are characterized by the nature of the photochemical transformation that corresponds to $M_1^* \rightarrow M_2$ in figure 1. In published work, we have been able to demonstrate the involvement of a potential surface topology of the form shown in figure 1 on most of these. The most common transformations, together with references to theoretical work in each are: a)Z,E cis trans isomerization [15, 17-27] b)pericyclic reactions [28-39] , c) tautomerization d) homolytic bond cleavage[40-52] and e) electron transfer.

In this short paper, we can only give some examples. . In reference [50] we report a detailed study of a model for the photochemical ring opening in spyropyran compounds



here the surface has exactly the form shown in figure 1. The TS in figure 1 corresponds to the C-O bond rupture on S_1 and leads to a conical intersection that is similar to that documented for the Paterno-Buchi reaction [41]. The essential point to make here is that the conical intersections associated with carbonyl ring closure reactions are all very similar the region of the conical intersection (CI in figure 1), we can find reaction paths to both the reactant minimum and the ring opened merocyanine product. Reactions involving double bond isomerization also have a similar topology and involve the same type of conical intersection [22] structure shown in figure 3

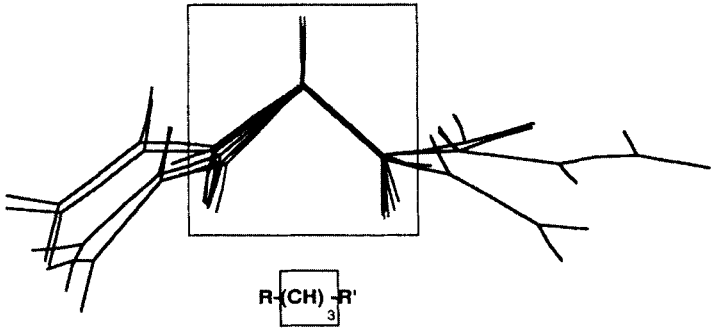


Figure 3 Geometry of the conical intersection in double bond isomerizations of polyenes.

The same conclusions can be drawn about the conical intersections in cycloadditions (compare reference 28 for 2+2 cycloadditions and the 4+4 results in reference 36,37)

CONCLUSIONS

In this short paper we have attempted to outline some of our work on photochemical and photophysical processes that are relevant to photochromic systems. We believe that the potential energy surfaces for these systems are now becoming quite well understood. The model of non-adiabatic processes occurring via a conical intersection seems to the ubiquitous in this subject. The theoretical tools and the experience in their use are well documented now. There seems no reason why this type of modelling approach cannot be applied with some considerable success in the design of photochromic systems.

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