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Introduction to the workshop on theoretical organic (photo)chemistry

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Abstract

The development of theoretical models for diabatic singlet photoreactions is briefly reviewed and recent advances and future aspects of organic photoreactions are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

This workshop was set up to review some recent advances and future aspects in the theoretical approach to the study of photochemical mechanisms. The goal of theory in this field is a complete description at the molecular level of photochemical and photophysical processes involving energy absorption, evolution of the system on one or more excited states and ultimately decay of the system back to the ground state. One of the challenging aspects of theoretical organic photochemistry is the description of diabatic transitions between the various excited states and the ground state of the system.

2. Theoretical models

In Fig. 1 some theoretical models for the discussion of organic ground state forbidden photoreactions are shown, which came up after the famous Woodward–Hoffmann rules [1] had been discovered. In the Zimmerman model (Fig. 1a) based on Hückel theory [2] the ground configuration and the HOMO–LUMO singly and doubly excited configurations are all degenerate at the pericyclic geometry. Van der Lugt and Oosterhoff [3], however, showed that by taking into account electron interaction, the crossing of the ground and doubly excited configurations will be avoided, leading to a ground state barrier and a "pericyclic minimum". The mechanism of a Woodward–Hoffmann allowed photoreaction, as, e.g. the $[2+2]$ cycloaddition or the butadiene to cyclobutene electrocyclic ring-closure reaction, was therefore concluded to consist of the following three steps: HOMO–LUMO excitation into the S_1 state, transition into the "pericyclic minimum" of a totally symmetric (mainly doubly excited) dark state, and finally internal conversion from the "pericyclic minimum" that acts as a funnel [4] back into the ground state, which can lead either to the product or back to the reactant, i.e. either a photochemical transformation or radiationless decay occurs.

A simple vibrational analysis at the "pericyclic minimum", however, reveals this geometry as a transition state rather than a minimum [5]. Following the normal coordinate that belongs to the imaginary frequency leads to a conical intersection, i.e. to a real crossing of the S_1 and S_0 surfaces that is not avoided.

At a conical intersection one can distinguish two directions $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ such that if the energy is plotted against these two variables (combinations of bond lengths, bond angles, etc.), the potential energy has the form of a double cone in the region of degeneracy as shown in Fig. 2a. The remaining $F-2$ directions, where F is the number of internal degrees of freedom, define the *intersection space* over which the energies of the two states are equal (Fig. 2b). A movement in the $(\boldsymbol{x}_1, \boldsymbol{x}_2)$ plane (the *branching space*) from a point on the intersection will result in the degeneracy being lifted. The two vectors $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ correspond to the gradient difference vector and to the diabatic coupling vector, respectively [6,7].

As conical intersections generally occur at geometries of lower symmetry than those used for the correlation diagrams [5], the Oosterhoff diagram of Fig. 1b corresponds to a plane through the double cone, which does not contain the intersection point. This situation is summarized in the theoretical model shown in Fig. 3 [7], which is based on the (2-in-2) model for biradicaloids due to Michl and co-workers [8]. The two planes shown describe a bonding

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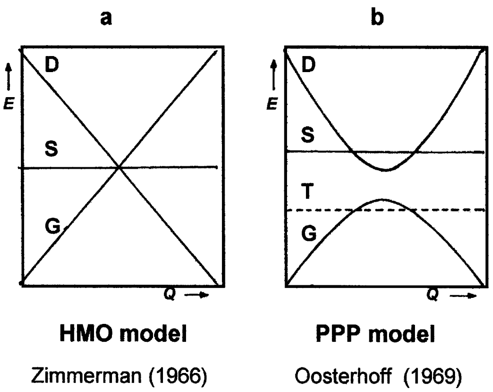

Fig. 1. Schematic correlation diagrams for ground state forbidden pericyclic reactions; (a) in the HMO model of Zimmerman [1] the correlation lines for the ground configuration G, as well as the HOMO → LUMO singly (S) and doubly (D) excited configurations meet all in one point, (b) in the PPP model of van der Lugt and Oosterhoff [3] the crossing of the ground and the doubly excited configurations is avoided, T denotes the triplet configuration (Adapted from [7]).

interaction between the nonbonding orbitals of a perfect biradical (homosymmetric case) and a polarizing perturbation corresponding to an electronegativity difference δ of the two orbitals (heterosymmetric case), respectively.

From the diagram it is seen that starting at the "pericyclic minimum" (perfect biradical with $\gamma = 0$, $\delta = 0$) the conical intersection is reached by applying an appropriate polarizing perturbation δ.

The role of a conical intersection in a photochemical reaction can be compared to that of a transition state in a thermal ground state reaction. An important difference, however, is that there is only one distinct direction that leads over the transition state to the product, while at the conical intersection the vectors $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ span a plane in which a number of reaction channels can open up. That is to say, several products may be reached from one conical intersection.

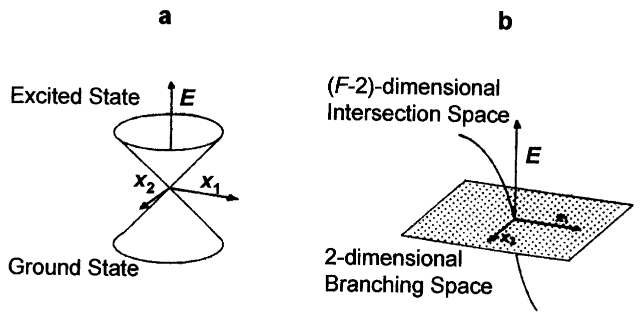

Fig. 2. Conical intersections; (a) two potential energy surfaces form a double cone if plotted against the gradient difference vector $\boldsymbol{x}_1 = \partial(E_1 - E_2)\partial\boldsymbol{q}$ and the nonadiabatic coupling vector $\boldsymbol{x}_2 = \langle Q_1|\partial Q_2/\partial\boldsymbol{q}\rangle$; (b) the vectors $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ span the "branching space" while the "intersection space" is a $(F-2)$-dimensional hyperline (adapted from [6]).

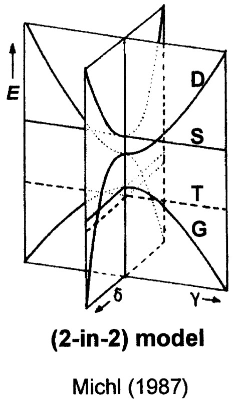

Fig. 3. Three-dimensional diagram based on the (2-in-2) model for biradicaloids of Bonacic-Koutecky et al. [8], exhibiting a real conical intersection. The two planes correspond to the homosymmetric (γ) and heterosymmetric (δ) case. For explanation of G, S, D and T see Fig. 1 (adapted from [7]).

3. Recent advances and future aspects

Although the fact that organic singlet photoreactions proceed via conical intersections has been firmly established during the last 10 years or so [9], and efficient computational methods to determine structures and energies at these conical intersections have been developed [10], it is not easy to predict the existence and the structure of a conical intersection without detailed calculations. Recently, however, based on the phase-change rule of Longuet-Higgins [11], a method which aims exactly at this goal has been proposed by Zilberg and Hass [12]. This will be discussed in the first contribution "Photochemistry by Conical Intersections: A Practical Guide for Experimentalists" by Y. Haas.

However, what we have to know in order to theoretically discuss photochemical reactivity is not only the loci of conical intersections, but information is also needed as to whether and how these areas on the potential energy surface can be reached, which requires the knowledge of excited state barriers and reaction paths. In addition, the various reaction paths on the ground state surface have to be characterized. The state of the art in this field will be discussed by M.A. Robb in his contribution "Theoretical Study of Mechanisms and Dynamics of Photochemical Processes: Complete Multi-State Reaction Paths and Non-adiabatic Dynamics".

One of the consequences of the fact that several reaction channels may open up at a single conical intersection is that on the basis of purely static calculations very little can be said about the quantitative yield of the various products. Thus, for a complete theoretical description of a photoreaction the dynamics of the reaction have to be studied as mentioned before. A full first-principles treatment of this problem requires a simultaneous solution of the electronic and nuclear Schrödinger equations, as is provided in the ab initio multiple spawning method of Ben-Nun and Martinez [13], who will in his contribution on "Photochemistry from First Principles: Advances and Future Aspects” assess the prospects of the method for modeling photochemistry in large molecules and condensed phases.

As very few photoreactions of practical importance are carried out in the gas phase, condensed phases are important and taking into account solvent effects in the theoretical description of organic photoreactions is therefore of major interest. This topic was to be covered by M. Zerner, whose untimely death on 2 February 2000 prevented this. As we thought it was not possible to replace him, we decided to dedicate this workshop to his memory. Ten years ago he published a key paper in this field [14], in which he showed that by modeling the protein as a solvent using the self-consistent reaction field (SCRF) method, the charge transfer state between the special pair and the bacteriopheophytin-*b* of the L branch of the photosynthetic reaction center from *Rhodopseudomonas viridis* is placed vibrationally accessible to the lowest excited state of the reaction center, thus enabling the charge separation which initiates the photosynthetic process. Recently, the polarizable continuum solvation model has been extended to the multi-configurational complete active space (MC-SCF) method and implemented in the Gaussian program by Robb and co-workers [15].

Another strategy for treating solvent effects is based on QC/MM molecular dynamics, that is on the combination of quantum chemistry and molecular mechanics, as, e.g. described by Berweger et al. [16] for the photoisomerization of *cis*-stilbene in solution. Finally, the Car–Parinello method [17] for the study of chemical reactions by means of first-principle dynamics based on density-functional theory has been suggested to be applicable to photochemical reactions of large systems [18].

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