The "Chemistry" of Conical Intersections

by Massimo Olivucci

In the Sixties chemists discover a multitude of fascinating photochemical organic reactions and the photochemistry of organic compounds rapidly became an independent branch of organic chemistry and technology. Despite this progress, only recently chemists has begun to understand the theory of photochemical reactions. An important contribution to this understanding has been achieved through the collaborative work of Olivucci (Università di Siena), Bernardi (Università di Bologna) and Robb (King's College London). For this reason their research project has been selected as one of the seven finalists of the 2001 edition of the Descartes Prize for the Scientific Excellence in Europe. The results of this research effort is described in the following.

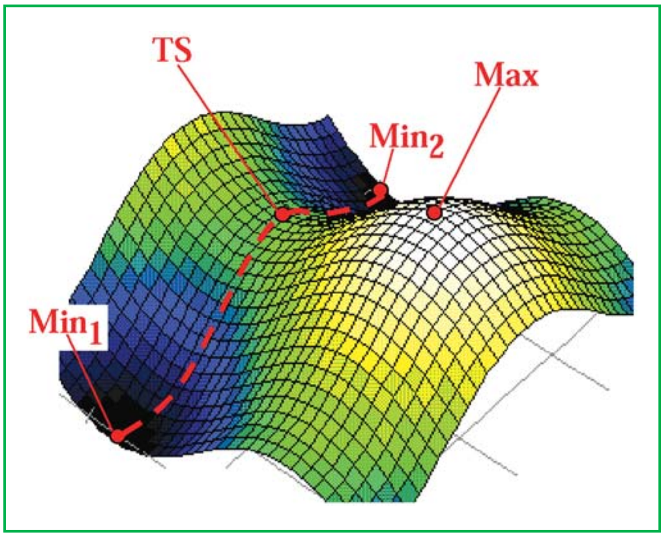


Figure 1 - Representation of the structure of the potential energy surface for a thermal chemical reaction

With their seminal 1935 work on the structure of potential energy surfaces, Eyring [1], Evans and Polaniy [2] were able to define the exact nature of the "activated complex" or "transition state" for ordinary (thermal) chemical reactions. The molecular structure of a transition state describes the spatial arrangement of the atoms corresponding to the highest point (TS) on the potential energy surface that has to be overcome by the reactant to form the product. This discovery not only provided the basic "conceptual tool" for understanding chemical reactivity, but also indicated the way for getting, through quantum chemical calculations, information on the molecular structure of the transition state. Furthermore the full reaction path can be determined by computing the minimum energy path (see dashed line in Figure 1): the curve that connects the transition state structure TS (a saddle point on the potential energy surface) with the energy minima associated with the reactant (Min$_1$) and the product (Min$_2$). The successful development of quantum chemistry packages and the availability of increasingly fast computers in more recent years have made the computational investigation of thermal reaction paths a routine practice in the modern chemical laboratory.

Before the project described in this article started, the computations of photochemical reaction paths was unpractical if not impossible. In a photochemical reaction the reactant is an electronically excited state molecule or complex M* while the product is a ground state species. Thus, in order to describe a *photochemical* reaction, one must first establish the nature of the spatial arrangement of the atoms corresponding to the point where M* decays from the excited state potential energy surface to the ground state and initiate product formation. Loosely, this critical molecular structure plays the role of the "transition state" for a photochemical process.

The classic text-book view of unsensitized (i.e. singlet) photochemical reactions is mainly due to the 1969 computational work of Van der Lugt and Oosteroff [3a]. These authors proposed that decay of M* takes place at an excited state energy minimum corresponding to an *avoided crossing* of the excited and ground state potential energy surfaces. However, experimental evidence such as the lack of fluorescence from such a minimum indicated that the decay must be extremely fast which can only occur when the energy gap between excited and ground state is few kcal mol^{-1}. On the other hand the calculation available at that time, which were forced to assume a fair degree of molecular symmetry all along the reaction path predicted quite sizable energy gaps [3 a,b]. In this conditions M* would rapidly equilibrate and the excited state decay would occur on a timescale close to that of fluorescence (i.e. allowing many vibrational oscillations) as in standard internal conversion processes.

In 1966 and 1972 Zimmerman [4] and Michl [5] were the first to suggest, independently, that certain photoproducts originate by decay of the excited state species M* through a conical intersection (CI) of the excited and ground state potential energy surfaces (see Figure 2). Zimmerman and Michl used the term "funnel" for this feature that corresponds, in contrast to the Van der Lugt and Oosteroff computation, to a *real* crossing of two potential energy surfaces. The same idea was proposed by Edward Teller [6] in 1969. Teller made two gen-

---

M. Olivucci, Dipartimento di Chimica - Università di Siena.
olivucci@unisi.it

eral observations: a) in a polyatomic molecule the non-crossing rule, which is rigorously valid for diatomics, fails and two electronic states, even if they have the same symmetry, are allowed to cross at a conical intersection; b) radiationless decay from the upper to the lower intersecting state occurs within a single vibrational period when the system “travels” in the vicinity of such intersection points. On the basis of these observations, Teller proposed that conical intersections provide a very fast decay channel from the lowest excited states of polyatomics which would explain the lack of fluorescence of the funnel. Despite the fact that the ideas of Teller, Zimmerman and Michl represented an important refinement of the avoided crossing model [3], *conical intersections were thought to be extremely rare or inaccessible* (i.e. located too high in energy) in organic compounds and thus were disregarded.

At the end of the Eighties improved ab initio quantum chemical methodologies became available which were suitable for computing, in a balanced way, excited and ground state potential energy surfaces. In particular the ab initio MC-SCF method had an analytical gradient which could be employed for efficient geometry optimization (the search for the structure corresponding to energy minima and transition states) taking into account the complete set of the 3N-6 nuclear degrees of freedom of the reacting system (N is the number of atoms). It was thus obvious that with this new methodology it was possible to overcome the limits (i.e. symmetry constraints and pre-defined reaction coordinate) used in the Van der Lugt and Oosteroff [3a] and Devaquet [3b] calculations.

A first application [9] of the ab initio MC-SCF method developed by M.A. Robb in 1990 to the photoinduced cycloaddition of two ethylene molecules showed that:

i) a conical intersection exists right at the bottom of the first excited state energy surface;
ii) the molecular structure of the conical intersection is related to the observed photoproducts and stereochemistry of the reaction.

Therefore it appeared clear that conical intersection could, contrary to the common belief and in agreement with Zimmerman [4], Michl [5] hypothesis, be frequent (if not ubiquitous) in organic systems. Further, they may constitute the photochemically relevant decay channel.

The hypothesis that conical intersections correspond to the decay bottleneck for photochemical processes also suggested that, similarly to thermal reactions, computation, via suitable quantum chemical methods, of their molecular structures could provide a rigorous way to define photochemical reaction paths. Such paths would have two branches. The first, excited state, branch corresponds to the minimum energy path connecting M^* (or the Franck-Condon structure FC) to the CI. The second, ground state, branch corresponds to the minimum energy path connecting the CI to the product energy minima P and P’ (see Figure 3).

The project. Search for conical intersections in organic chromophores

Despite the hypothesis of Zimmerman [4] and Michl [5] as well as few encouraging computational results by Michl and coworkers [7, 8] and by ourselves [9] there is no general theorem supporting the existence of low-lying (i.e. accessible in ordinary experimental conditions) conical intersections in organic chromophores. *The only way to prove the validity of the hypothesis stated above was a painstaking systematic search for properties i-ii in different classes of organic chromophores.*

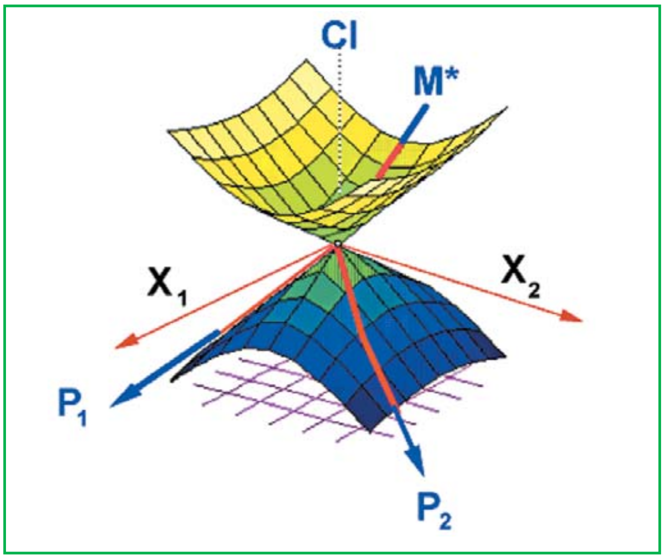


Figure 2 - Structure of a conical intersection along the X1,X2 branching plane. A schematic M→P1,P2 reaction path is also shown*

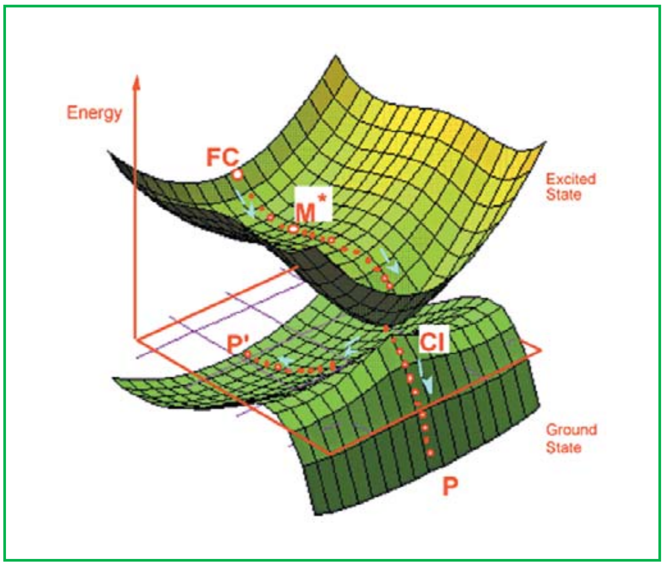


Figure 3 - Representation of the general structure of a photochemical reaction path

In 1992 our research teams (Bernardi and Olivucci in Bologna and Robb in London) started a long-term research project with an investigation of the simplest organic chromophores: olefines, isolated and conjugated dienes (see ref. 10-12 in Appendix). In all cases we used the ab initio MC-SCF quantum chemical method developed by Robb for evaluating the excited and ground state energy and the corresponding gradients. Between 1992 and 2000 the potential energy surfaces of ca. 25 different organic chromophores were mapped to search for photochemically relevant conical intersections (see Section B in Appendix). The compounds belong to one of the following classes:

- Cromophores with one double-bond (or two isolated double bonds)

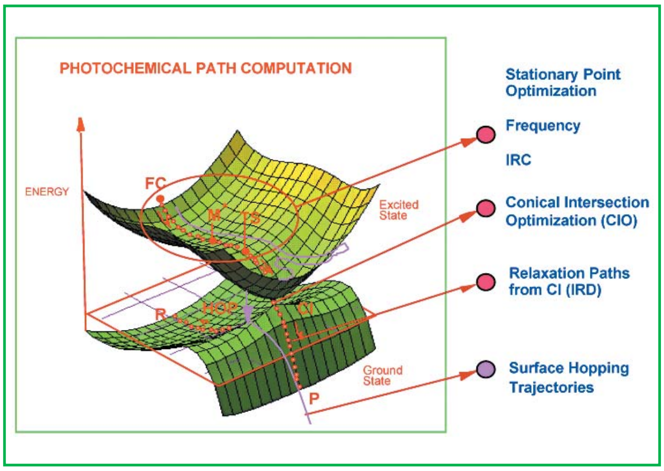


Figure 4 - Computational methods available for studying photochemical reactions

Table 1

Reaction	*Ref. in Appendix*
Ring-opening and ring-closure	10, 11, 15-17, 19, 20, 25, 43, 53
[1,2], [1,3] Sigmatropic shifts	11, 14
Di-π-methane rearrangement	13
Oxa-di-π-methane rearrangement	45
Valence isomerization of aromatics	30, 35
[2+2], [4+2] and [4+4] Cycloadditions	32, 24, 27
Bicyclization of dienes	28
Cis-trans isomerization	18, 43, 48-52
Deazetization	37, 39, 42
Hydrogen transfer	38, 40
Charge transfer	41
Paterno-Buchi	44
Polysilane fragmentation	47

- Cromophores with conjugated double-bonds
- Aromatic chromophores and related compounds
- Azo-chromophores
- Chromophores with a carbonyl group or a conjugated carbonyl group
- Polysilanes
- Models of the retinal chromophore (Schiff bases)
- Model photochromic compounds and dyes.

Such a systematic investigation could not be carried out without the development of more efficient and novel computational tools (see Section A in Appendix). The first tool developed was a method (the CIO method) for the automatic and unbiased search and optimization of low-lying conical intersection points between pairs of potential energy surfaces (ref. 1 in Appendix). Other novel tools were designed and implemented to determine the ground state branch of photochemical reaction paths (the IRD method in ref. 5 of Appendix) and to compute "photochemical" semi-classical trajectories (ref. 6 and 9 in Appendix) i.e. trajectories that start on the excited state energy surface and hops to the ground state surface in the region of the conical intersection. With the help of these tools a complete computational strategy was defined to compute the entire photochemical reaction path (ref. 2, 4 and 7). The traditional (e.g. Stationary point search, Frequency and IRC computations) and new mapping methods used in our project are schematically summarized in Figure 4. Notice that *the CIO, IRD and Surface Hopping Trajectory methods (ref. 1, 5 and 6 respectively in Appendix) have been designed and implemented within the present project.*

In dealing with the conical intersections of large conjugated organic chromophores (e.g. the [18] annulene of ref. 36 or the long polyene chains of ref. 29) that could not be investigated with the expensive MC-SCF method, we used our hybrid QM/MM method (the MM-VB method. See ref. 3 and 8 in Appendix). This method was designed by Olivucci, Bernardi and Robb and parametrized to reproduce the results of MC-SCF calculations [10].

Role of the research teams. An European network

The research teams (M.A. Robb at King's College London and F. Bernardi and M. Olivucci at the University of Bologna and, more recently, at the University of Siena) have been working in tight collaboration and exclusively within the European Community.

Robb's theoretical chemistry group has mainly focused on the methodological and photophysical aspects of the project. Thus this group has implemented the majority of the new methods (Section A in Appendix) and carried out the corresponding benchmarking and tuning. These tools have been used by the computational/theoretical organic chemistry groups of Bernardi and Olivucci to carry out the mapping of potential energy surfaces of a series of selected organic chromophores. During the project many students and Post-Doc have been involved in the research work and exchanged between the two teams. This fruitful collaborative effort has been recognized at the national level. M.A. Robb has been appointed Fellow of the Royal Society in 2000. F. Bernardi has been awarded the 2000 Mangini Medal by the Italian Chemical Society and M. Olivucci has been awarded the Italian "Premio Nazionale Federchimica" in 1999.

Results: conical intersections in photochemistry, photophysics and photobiology

The main result of the project is that low-lying conical intersections have been located and characterized for all the investigated systems. This finding strongly support the hypothesis that low-lying conical intersections are ubiquitous in organic molecules.

The molecular structure of the computed conical intersection is related to the structure of the observed photoproducts pretty much in the same way in which, for a thermal reaction, the transition state structure is related to the molecular structure of the product. This relationship supports the validity of conical intersections as key mechanistic elements in organic photochemistry. Our computations (see part B in Appendix) support the above statement for the photochemical reactions reported in Table 1.

Conical intersection has also been shown to provide the decay channel associated with photophysical processes such as the ultrafast (usually subpicosecond) radiationless deactivation and quenching of excited states (Table 2).

For instance, in the first (π-π^*) excited state (S_1) of benzene there is a ~3,000 cm^{-1} threshold for the disappearance of S_1 fluorescence. This observation is assigned to the opening of a very efficient, radiationless decay channel (termed "channel 3") leading to the production of fulvene and benzvalene. Our ab initio MC-SCF computations show that the potential energy surface of S_1 is consistent with that of Figure 3 and 4. Thus the observed energy threshold (which is computed using the more accurate multireference MP2 computations) corresponds to the barrier that separates S_1 benzene from the conical intersection of Figure 5. By examining the molecular structure of this conical intersection, one can derive information on benzene reactivity. For instance, it is obvious from the structure that the kink feature (framed area in Figure 5) suggests formation of a cyclopropyl ring upon decay to the ground state. Thus the "primary" photoproduct of the reaction is predicted to be a diradical species characterized by a 1,3-transanular bond. This structure corresponds with to pre-fulvene which was previously proposed as the intermediate in fulvene/bezvalene production (see Scheme 1).

The example of benzene shows that the same conical intersection may mediate both photophysical (i.e. fast radiationless deactivation. For instance, in azulene the well-known lack of S_1 fluorescence is due to a specific conical intersection. See Ref. 33 in Appendix) and photochemical processes. The rate of these processes is controlled by the magnitude of an excited state barrier (a conventional TS) located between the excited state reactant and the conical intersection. We reported computational evidence that when the barrier is very small or negligible the corresponding deactivation (or chemical reaction) is ultrafast (see ref. 58, 59 in Appendix).

As mentioned above one of the major results of our work is the efficient and unbiased computation of the molecular structure of diverse conical intersections. Inspection of these structures leads to two general conclusions:

i) *related organic chromophores (e.g. linear and cyclic conjugated hydrocarbons) have similar conical intersection structures.* As an example one can compare the conical intersection structure of linear polyenes (butadiene, hexatriene etc. - see Figure 6 for octatetraene) and polyene radicals (allyl, pentadienyl etc.) with the conical intersection structure of benzene. These structures are characterized by the same kink feature (the framed triangular arrangement with three weakly interacting π-electrons). This kink structure prompts cis-trans isomerization and valence isomerization in polyenes (ref. 18, 20-21, 23, 29 in Appendix) and aromatics (ref. 31, 35 in Appendix) respectively.

ii) *all basic chemical events such as bond breaking, bond forming and group exchange can be mediated by conical intersections*. The conical intersection for the hydrogen atom transfer between a chlorinated hydrocarbon (CH_2Cl_2) and an azoalkane (pyrazoline) shows a hydrogen still "moving" between the two fragments (see Figure 7). Clearly the chemical event is not completed on the excited state but is interrupted halfway along the reaction coordinate by the conical intersection (ref. 38, 40 in Appendix).

Table 2

Ultrafast radiationless decay	*Ref. in Appendix*
Polyenes and polyene Schiff bases	21, 23, 29
Benzene	30
Azulene	33
Fulvene	34
Indacene	36
Cyanines	54
Styrene	31
Quenching	*Ref. in Appendix*
n-π^* states/chlorinated hydrocarbons	38
n-π^* states/amines	41

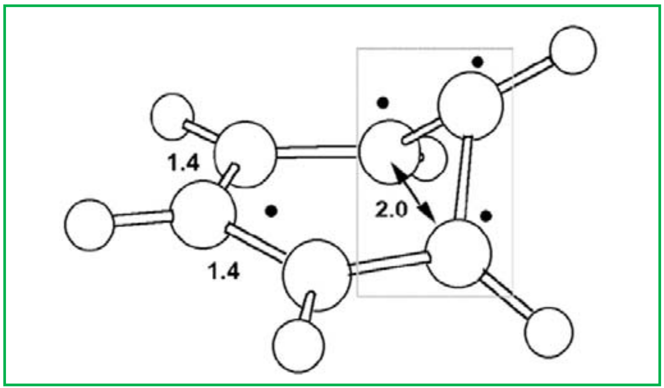
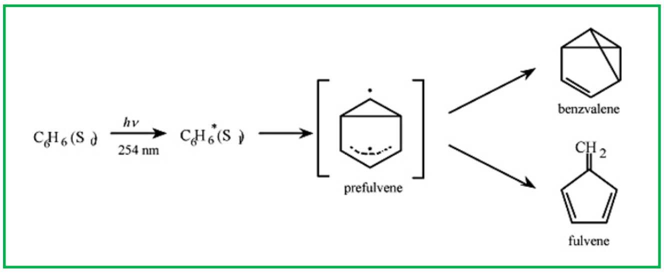


Figure 5 - The structure of the conical intersection of benzene



Scheme 1

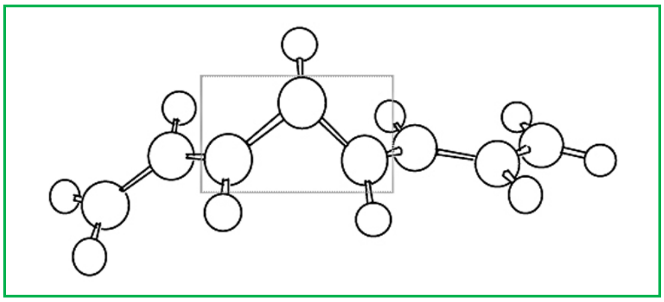


Figure 6 - The structure of the conical intersection of a linear polyene

An outstanding result achieved during the project, is the demonstration that conical intersections control (ultrafast) photobiological reactions. The methods developed by our teams have been capable to provide information on the mechanism of the primary event in vision. Using a realistic model of the retinal chromophore (Scheme 2) of rhodopsin (the human retina visual pigment) we have demonstrated that a conical intersection featuring a 90° twisted retinal structure controls the decay to the ground state and initiate the protein photocycle. (ref. 51, 52 in Appendix). Ab initio semi-classical trajectory calculations have been carried out on a computationally less expensive model to investigate the time-dependent structural changes in retinal and to estimate the reaction time-scale (ref. 49 in Appendix). The results shows that, indeed, these type of chromophores reach the conical intersection in the subpicosecond time-scale.

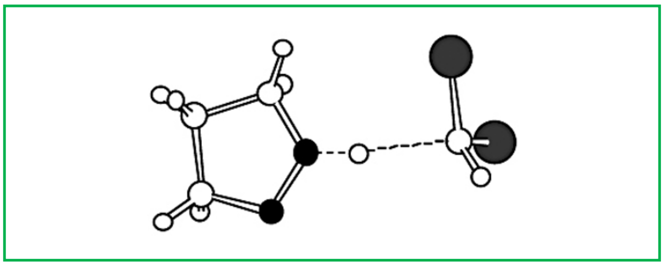
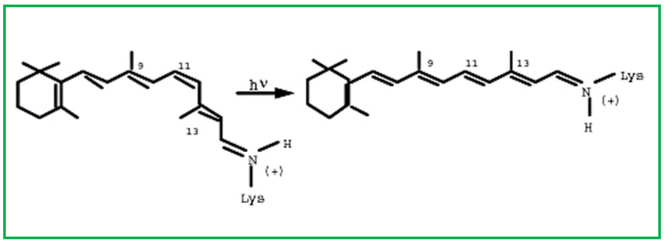


Figure 7 - The structure of the conical intersection for an hydrogen atom exchange



Scheme 2

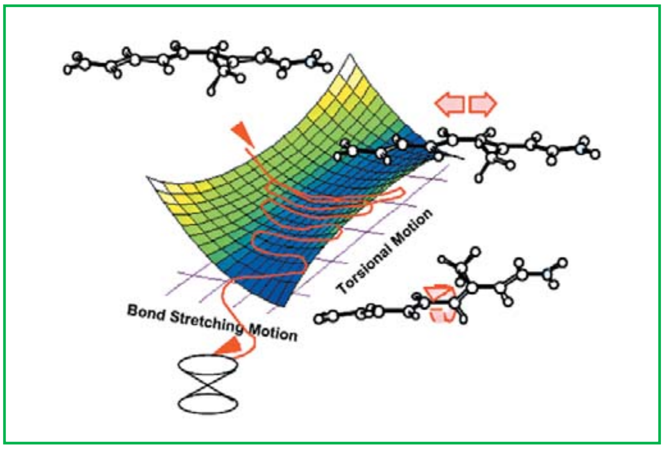


Figure 8 - The structure of the excited state potential energy surface for a "realistic" model of protonated Schiff base of retinal (the human retina chromophore)

We have also been able to determine the nature of the excited state reaction coordinate controlling the motion towards the conical intersection (CI). The computed coordinate (see Figure 8) involves a sequential evolution along two different modes as first proposed by Ottolenghi for bacteriorhodopsin [11]. The initial mode corresponds to the stretching of the double bonds that are thus prepared for facile torsional deformation. This initial evolution is indeed followed by torsional motion about a double bond that invariably leads to decay at a conical intersection. Such a "two-mode" coordinate, has now been experimentally confirmed for different types of rhodopsins (see ref. 12, 13 for bovine rhodopsin).

Impact and perspectives: towards a computer-aided design of photochemical processes

Our systematic study demonstrates that conical intersections are (in analogy with transition states) a critical mechanistic elements in "direct" photochemistry (including ultrafast radiationless deactivations and biological photoisomerizations). For sensitized photochemistry, which is usually dominated by triplet excited states we have shown that the same methods used for mapping conical intersections can be used to locate triplet/singlet crossings which dominates these reactions (see for instance ref. 43-46 in Appendix). While the replacement of the text-book concept of avoided crossing with that of conical intersection can be seen as a refinement of the idea of funnel, we have demonstrated that, in practice, only the conical intersections lie along excited state reaction coordinates and therefore provide a rigorous basis for the construction of photochemical reaction paths.

The developments of tools for constructing photochemical reaction paths (see Figure 4 above), their availability in commercial quantum chemical packages (such the Gaussian98 package were a CIO method has been implemented by M.A. Robb) and the computational strategies now reported in different review articles (see ref. 60-63 in Appendix) provide a solid basis for a widespread use of computational chemistry in tackling photochemical problems. Our work in the field of photochromic compounds and cyanine dyes (see Section B.8 in Appendix) show that the emerging field of computational photochemistry may successfully be applied to the computer-aided design of novel photo-reactive materials. Needless to say that the full implementation of these demanding methods will be boosted in future years by the continuous increase in computer performance and availability of more efficient software technology.

References

[1] H. Eyring, *Chemical Reviews,* 1935, **XVII,** 65.
[2] M. Evans, M. Polaniy, *Transaction of the Faraday Society,* 1935, **XXXI,** 875.
[3] a) W.T.A.M. van der Lugt, L.J. Oosterhoff, *J. Am. Chem. Soc.,* 1969, **91,** 6042; b) D. Grimbert *et al., J. Am. Chem. Soc.,* 1975, **97,** 6629.
[4] H.E. Zimmerman, *J. Am. Chem. Soc.,* 1966, **88,** 1566.
[5] J. Michl, *J. Mol. PhotoChem.,* 1972, 243 and 257.
[6] E. Teller, *Isr. J. Chem.,* 1969, **7,** 227.
[7] W. Gerhartz *et al., J. Am. Chem. Soc.,* 1976, **98,** 6427.
[8] W. Gerhartz *et al., J. Am. Chem. Soc.,* 1977, **99,** 4263.
[9] F. Bernardi *et al., J. Am. Chem. Soc.,* 1990, **112,** 1737.
[10] F. Bernardi *et al., J. Am. Chem. Soc.,* 1992, **114,** 1606.
[11] Q. Zhong *et al., J. Am. Chem. Soc.,* 1996, **118,** 12828.
[12] T. Kakitani *et al., J. Phys. Chem. B,* 1998, **102,** 1334.
[13] G. Haran *et al., J. Phys. Chem. A.,* 1999, **103,** 2202.

Appendix

A) Design and implementation of novel computational tools

[1] Optimization and characterization of the lowest energy point on a conical intersection using an MC-SCF Lagrangian, I.N. Ragazos *et al., Chem. Phys. Lett.,* 1992, **197,** 217.
[2] Modelling Photochemical Reactivity of Organic Systems - A New Challenge to Quantum Computational Chemistry, F. Bernardi *et al., Israel Journal of Chemistry*, 1993, **33,** 265.
[3] Molecular Mechanics Valence Bond Methods for Large Active Spaces. Application to Conjugated Polycyclic Hydrocarbons, M.J. Bearpark *et al., Chem. Phys. Lett.,* 1994**, 217,** 513**.**
[4] Following Reaction Paths in Organic Photochemistry: The Special Role of Surface Crossings, F. Bernardi *et al., Pure & Appl. Chem.,* 1995, **67,** 17.

[5] Geometry Optimization on a Hypersphere. Application to Finding Reaction Paths from a Conical Intersection, O. Celani *et al., Chem. Phys. Lett.,* 1995, **243,** 1.

[6] Classical Wavepacket' Dynamics through a Conical Intersection. Application to the S1/S0 Photochemistry of Benzene, B.R. Smith *et al., Chem. Phys. Lett.,* 1995, **242,** 27.

[7] Application of Computational Chemistry to the Modelling of Organic Reactivity in Ground and Excited States, M.A Robb *et al.,* AIP Conference Proceedings 330 - E.C.C.C. 1 Computational Chemistry, 1995.

[8] Benchmarking the Molecular Mechanics-Valence Bond Method: Photophysics of Styrene and Indene, M.J. Bearpark *et al., J. Phys. Chem. A,* 1997, **101,** 8395.

[9] Mixed State "on the fly" Non-adiabatic Dynamics: the Role of the Conical Intersection Topology, S. Klein *et al., Chem. Phys. Lett.,* 1998*,* **292,** 259.

B) Conical Intersections in Organic Chromophores

B.1 Cromophores with one double-bond (or isolated double bonds)

[10] Origin of the Nonstereospecificity in the Ring Opening of Alkyl-Substituted Cyclobutenes, F. Bernardi *et al., J. Am. Chem. Soc.,* 1992, **114,** 2752.

[11] Can a Photochemical Reaction Be Concerted? A Theoretical Study of the Photochemical Sigmatropic Rearrangement of But-1-ene, F. Bernardi *et al., J. Am. Chem. Soc.,* 1992, **114,** 5805.

[12] An MC-SCF study of the Thermal and Photochemical Cycloaddition of Dewar Benzene, I.J. Palmer *et al., J. Org. Chem.,* 1992, **57,** 5081.

[13] A Concerted Nonadiabatic Reaction Path for the Singlet Di-π-methane Rearrangement, M. Raguero *et al., J. Am. Chem. Soc.,* 1993**, 115,** 2073.

[14] Falling Down the Singlet Manifold. A CAS-SCF Mechanistic Study of the Far-UV Photochemistry of Hexa-1,5-dienes, I. Rossi *et al., J. Phys. Chem.,* 1995, **99,** 6757.

B.2 Cromophores with conjugated double-bonds

[15] A New Mechanistic Scenario for the Photochemical Transformation of Ergosterol: an MC-SCF and MM-VB Study, F. Bernardi *et al., J. Am. Chem. Soc.,* 1992, **114,** 8211.

[16] A Conical Intersection Mechanism for the Photochemistry of Butadiene, M. Olivucci *et al., J. Am. Chem. Soc.,* 1993, **115,** 3710.

[17] Substituent Effects in Buta-1,3-diene Photochemistry: A CAS-SCF Study of 2,3-Dimethylbutadiene and 2-Cyanobutadiene Excited-State Reaction Paths, M. Olivucci *et al., J. Am. Chem. Soc.,* 1994, **116,** 2034**.**

[18] Excited-State Cis-Trans Isomerization of cis-Hexatriene. A CAS-SCF Computational Study, M. Olivucci *et al., J. Am. Chem. Soc.,* 1994, **116,** 1077.

[19] What Happens during the Picosecond Lifetime of $2A_1$ Cyclohexa-1,3-diene? A CAS-SCF Study of the Cyclohexadiene/Hexatriene Photochemical Interconversion, P. Celani *et al., J. Am. Chem. Soc.,* 1994, **116,** 10141.

[20] Excited-state Reaction Pathways for *S-cis* Buta-1,3-diene, P. Celani *et al., J. Am. Chem. Soc.,* 1995, **102,** 5733.

[21] Molecular "Trigger" for Radiationless Deactivation of Photoexcited Conjugated Hydrocarbons, P. Celani *et al., J. Am. Chem. Soc.,* 1995, **117,** 11584.

[22] Do Photochemical Ring-Openings Occur in the Spectroscopic State? 1B2 Pathways fot the Cyclohexadiene/Hexatriene Photochemical Interconversion, P. Celani *et al.,* J. Phys. *Chem.,* 1996, **100,** 19364.

[23] The Structure of the Nonadiabatic Photochemical *Trans*→*Cis* Isomerization Channel in *All-Trans* Octatetraene, M. Garavelli *et al., J. Am. Chem. Soc.,* 1996, **118,** 11656.

[24] Modeling Photochemical [4+4] Cycloadditions: Conical Intersections Located with CASSCF for Butadiene + Butadiene, M.J. Bearpark *et al., J. Am. Chem. Soc.,* 1997, **119,** 709.

[25] Relaxation Paths from a Conical Intersection: The Mechanism of Product Formation in the Cyclohexadiene/Hexatriene Photochemical Interconversion, M. Garavelli *et al., J. Phys. Chem.,* 1997, **101,** 2023.

[26] Cooperating Rings in *cis*-Stilbene Lead to an S_0/S_1 Conical Intersection, M.J. Bearpark *et al., J. Phys. Chem. A,* 1997, **101,** 3841.

[27] Product Distributions from Molecular Mechanics-Valence Bond Dynamics: Modeling Photochemical [4+4] Cycloadditions, M. Deumal *et al., J. Org. Chem.,* 1998, **63,** 4594.

[28] Photochemistry of Highly Alkylated Dienes: Computational Evidence for a Concerted Formation of Bicyclobutane, M. Garavelli *et al., J. Am. Chem. Soc.,* 1999, **121,** 1537.

[29] Relaxation Paths and Dynamics of Photoexcited Polyene Chains: Evidence for Creation and Annihilation of Neutral Soliton Pairs, M. Garavelli *et al., J. Am. Chem. Soc.,* 2000, **122,** 5568.

B.3 Aromatic Chromophores and Related Compounds

[30] An MC-SCF study of the S_1 and S_2 photochemical reactions of benzene. A MC-SCF study, I.J. Palmer *et al., J. Am. Chem. Soc.,* 1993, **115,** 673.

[31] An MC-SCF Study of Styrene Singlet-State Photoisomerization, M.J. Bearpark *et al., J. Am. Chem. Soc.,* 1995, **117,** 6944.

[32] Conical Intersection Pathways in the Photocycloaddition of Ethene and Benzene, M.J. Bearpark *et al., J. Am. Chem. Soc.,* 1996, **118,** 7353.

[33] The Azulene S1 State Dynamics via a Conical Intersection: A CASSCF Study with MMVB Dynamics, M.J. Bearpark *et al., J. Am. Chem. Soc.,* 1996, **118,** 169.

[34] Can Fulvene S_1 Decay Be Controlled? A CASSCF Study with MMVB Dynamics, M.J. Bearpark *et al., J. Am. Chem. Soc.,* 1996, **118,** 5254.

[35] Annulene: a benzene-like S_0/S_1 conical intersection located with CASSCF + GVB, M.J. Bearpark *et al., Mol. Phys.,* 1996, **89,** 37.

[36] Characterisation of the Indacene S_0/S_1 Conical Intersection. An MMVB and CASSCF study, M.J. Bearpark *et al., Mol. Phys.,* 1999, **96,** 645.

B.4 Azo-Chromophores

[37] Mechanism of Carbene Formation from the Excited State of Diazirine and Diazomethane: An MC-SCF Study, N. Yamamoto *et al., J. Am. Chem. Soc.,* 1994, **116,** 2064**.**

[38] The Mechanism for the Solvent-Induced Quenching of Singlet-Excited Azoalkanes: Evidence for Thermally Activated Hydrogen Abstraction and Deactivation through a Conical Intersection, W.M. Nau *et al., Ang. Chem. Int. Ed.,* 1998, **37,** 98.

[39] An MC-SCF/MP2 Study of the Photochemistry of 2,3-Diazabicyclo[2.2.1]hept-2-ene: Production and Fate of Diazenyl and Hydrazonyl Biradicals, N. Yamamoto *et al., J. Am. Chem. Soc.,* 1998, **120,** 2391.

[40] Discrimination between Hydrogen Atom and Proton Abstraction in the Quenching of n,π^* Singlet-Excited States by Protic Solvents, W.M. Nau *et al., Ber. Bunsenges. Phys. Chem.,* 1998, **102,** 486.

[41] Conical Intersections in Charge-Transfer Induced Quenching, A. Sinicropi *et al., Ang. Chem. Int. Ed.,* 2000, **39,** 4582.

[42] An ab initio study of the Photochemical Decomposition of 3,3-Dimethyldiazirine, F. Bernardi *et al., J. Org. Chem.,* 2000, **65,** 7847.

B.5 Chromophores with a carbonyl group or a conjugated carbonyl group

[43] Excited-State Potential Surface Crossings in Acrolein: A Model for Understanding the Photochemistry of α,β-Enones, M. Reguero *et al., J. Am. Chem. Soc.,* 1994, **116,** 2103**.**

[44] An MC-SCF Study of the (Photochemical) Paterno-Buchi Reaction, I.J. Palmer *et al., J. Am. Chem. Soc.,* 1994, **116,** 2121.

[45] Mechanism of the Oxadi-π-methane and [1,3]-Acyl Sigmatropic Rearrangements of β,γ-Enones: A Theoretical Study, S. Wilsey *et al., J. Am. Chem. Soc.,* 1996, **118,** 176.

[46] The Role of Degenerate Biradicals in the Photorearrangement of Acylcyclopropenes to Furans, S. Wilsey *et al., J. Am. Chem. Soc.,* 1996, **118,** 4465.

B.6 Polysilanes

[47] Mechanism of Photodegradation of Polysilanes: A Relaxed Cross Section of the Conical Intersection Hyperline in 2-Methyltrisilane, A. Venturini *et al., Organometallics,* 1995, **14,** 4953.

B.7 Models of the retinal chromophore (Schiff bases)

[48] The $C_5H_6NH_2(+)$ Protonated Schiff Base: an Ab initio “Minimal” Model for Retinal Photoisomerization, M. Garavelli *et al., J. Am. Chem. Soc.,* 1997, **119,** 6891.

[49] *Ab initio* Photoisomerization Dynamics of a Simple Retinal Chromophore Model, T. Vreven *et al., J. Am. Chem. Soc.,* 1997, **119,** 12687.

[50] The Short-Chain Acroleiniminium and Pentadieniminium Cations: towards a Model for Retinal Photoisomerization. A CASSCF/PT2 Study, M. Garavelli *et al., Theochem,* 1999, **463,** 59.

[51] Photoisomerization Path for a Realistic Retinal Chromophore Model: the Nonatetraenimminium Cation, M. Garavelli *et al., J. Am. Chem. Soc.,* 1998, **120,** 1285.

[52] Computational Evidence in Favour of a Two-State Two-Mode Model of the Retinal Chromophore Photoisomerization, R. Gonzalez-Luque *et al., Proc. Nat. Acad. Sci USA,* 2000, **97,** 9379.

B.8 Model photochromic compounds and dyes

[53] Conical Intersection Mechanism for Photochemical Ring Opening in Benzospiropyran Compounds, P. Celani *et al., J. Am. Chem. Soc.,* 1997, **119,** 10815.

[54] Ultrafast Radiationless Deactivation of Organic Dyes: Evidence for a Two-state Two-mode Pathway in Polymethine Cyanines, A. Sanchez-Galvez *et al., J. Am. Chem. Soc.,* 2000, **112,** 2911.

C) Conical intersections in photochemistry and photophysics

[55] Potential Energy Surface Crossings in Organic Photochemistry, F. Bernardi *et al., Chem. Soc. Rev.,* 1996, **25,** 321.

[56] Conical Intersection in the Theory of Organic Photochemistry, F. Bernardi *et al., The Spectrum,* 1996, **9,** 1.

[57] The Role of Conical Intersections and Excited State Reaction Paths in Photochemical Pericyclic Reactions, F. Bernardi *et al., J. Photochem. Photobiol. A: Chemistry,* 1997, **105,** 365.

[58] Force Fields for “Ultrafast” Photochemistry: the $S_2(1Bu)\rightarrow S_1(2Ag)\rightarrow S_0(1Ag)$ Reaction Path for *all-trans*-hexa-1,3,5-triene, M. Garavelli *et al., J. Am. Chem. Soc.,* 1997, **119,** 11487.

[59] Potential-Energy Surfaces for Ultrafast Photochemistry. Static and Dynamic Aspects, M. Garavelli *et al., Faraday Discussion,* 1998, **110,** 51.

[60] Photochemistry, M.A. Robb *et al., Encyclopedia of Computational Chemistry,* 1998, **3**.

[61] The Molecular Mechanics Valence Bond Method. Electronic Structure and Semiclassical Dynamics: Applications to Problems in Photochemistry, M.J. Bearpark *et al., Combined Quantum Mechanical and Molecular Mechanical Methods, ACS Symposium Series,* 1198, **712,** 148.

[62] A Computational Strategy for Organic Photochemistry, M.A. Robb *et al., Reviews in Computational Chemistry*, 2000, **15,** 87.

[63] Calculation of Excited State Conformational Properties, M. Olivucci *et al., Conformational Analysis of Molecules in Excited States,* 2000, 297.