

FINAL REPORT: ANALYSIS OF THE ROLE OF THE CONICAL INTERSECTION SEAM IN ETHENE+ETHENE AND ETHENE+BENZENE PHOTOCHEMICAL REACTIONS

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Summary

The objective of the project was to analyse the role of conical intersection (CI) seams in photochemical processes. As we already highlighted in the “mid-term” report, we decided to postpone the study of intramolecular proton transfer, since it is known that there are three states involved in the mechanism (and hence a 3-state conical intersection), and focus on a problem in which there are just 2 states involved, but multiple coordinates, to test and experiment with the new code developed by our group to analyse conical intersection seams at second order (F. Sicilia et al., J Chem Theory Comput. 2008, 4, 257). Such a problem is, indeed, very important in industry: photocycloadditions, specifically ethene+ethene and benzene+ethene, and to investigate substituent effects.

During the project we have analysed firstly the model system ethene+ethene, as a benchmark and training about how to use the new code (published in J.J. Serrano-Perez, DOI: 10.1080/00268976.2012.698757). In addition, the use of valence-bond (VB) theory helped us to understand the meaning of the crossing seam. This learning was priceless to face the more complex benzene+ethene system, in which not only the seam was proved to be important, but also the connections among multiple structures on the excited singlet state as well as the ground state. Specifically, we were forced to use non-standard techniques in order to obtain a picture of the photochemical panorama of this transformation (paper submitted to J. Org. Chem.). Finally, a study about the photocycloaddition of benzene with substituted alkenes is currently in progress.

On the other hand, following the grant application, the researcher has attended some courses at Imperial College London in order to develop the skills to become a senior researcher and a group leader in the foreseeable future (e.g. Preparing successful research funding applications, Introduction to Project Management for Postdoctoral Research Staff, Stepping Up to Management, Planning and Managing Research). Besides this, the fellow has been involved in other research projects, teaching duties and supervision of visiting students (Mrs. Aurelie Perveaux, currently at University of Montpellier, and Mr. Antoine Herzog, from Ecole polytechnique fédérale de Lausanne).

Research objectives

Modern theoretical photophysics and photochemistry are based on the study of the potential energy hypersurfaces of the electronic states given that they are the playground in which physical and chemical phenomena take place. Indeed, every photophysical and photochemical process is produced owing to the relations between the hypersurfaces of the electronic states which contribute to that process. It is important to characterize the most relevant stationary points (minima, transition states...) of the PES related to the lowest-lying excited states, as well as to define the paths from the reactants to the products through all the electronic states involved using MEPs (minimum energy paths).

For the specific case of close degeneracies between the surfaces, where ultrafast energy transfers take place, the Born-Oppenheimer approximation breaks down and we need special methods in order to localize, optimize and study the crossing structures. In general, these crossings are named conical intersections (CI), and they are used in the rationalization of chemical processes where the pathway involves more than one single potential energy surface. In the past two decades conical intersections have been shown to play a central role in our understanding of photochemical reactions. CI structures provide gates for fast radiationless transitions and they are the cornerstone in many photochemical processes. The nature and topology of the CI are also important to determine the fate of the absorbed energy and the molecular transformations involved, i.e., the nature and yield of the possible photoproducts, or the photostability of the ground state, or the emission or not of energy as light. In this regard, the topology of a conical intersection may be peaked or sloped, being the former ones more efficient as

funnels. Therefore it is not only important to compute the energy of a given CI, but also to determine its accessibility from the S1 PES (i.e. if the CI is conformationally and energetically accessible from the initially populated excited state) as well as its topology.

Photocycloadditions have been studied in depth in the last decades, and many authors have tried to rationalize them (Woodward-Hoffmann, Van der Lugt-Oosterhoff, Michl...). Since the 1990s it was clear that the role of crossing structures was crucial to understand these processes. In essence, a photochemical reaction path has two segments: a branch on the excited state and a branch on the ground state. The two segments are connected at a point where the potential energy surfaces become degenerate (CI). However, a conical intersection is not an isolated point but a collection of points which we will refer to as a seam. The analysis of the conical intersection seam in these systems has been carried out using the aforementioned second-order method of Sicilia et al., via CASSCF computations in which the curvature of the intersection space at a critical point is determined from analytic second derivatives. Therefore it is possible to characterize these stationary points as minima or saddle points, and the vibrational modes corresponding to any imaginary frequencies can be used to suggest connections among CI points (i.e., if they belong to the same branch or to different branches of the S₁/S₀ seam). In addition, we can carry out seam-MEPs in the seam, and all the points computed along this coordinate have to satisfy two independent conditions: i) at each of these points the intersection-space gradient must be tangential to the crossing seam, and ii) at all the computed geometries, the two crossing electronic states must be degenerate.

Three cycloaddition modes (regioselectivity) can be distinguished (see Figure 1): ortho-cycloaddition [1,2], meta-cycloaddition [1,3], and para-cycloaddition [1,4]. The photocycloaddition reactions of arenes with alkenes have been extensively studied in order to rationalize the formation of the three possible cycloaddition products. The meta-cycloaddition mode ([1,3] in our simplified notation) has been applied most extensively and is used as an important step in the synthesis of natural products. This is the usual outcome in the photocycloadditions of arenes + alkenes. The ortho [1,2] product is found experimentally in reactions involving arenes with electron-withdrawing substituents. Ortho addition is preferred when there is a substantial difference between the electron-donor and electron-acceptor properties of the arene and the alkene, and meta when these differences are small. Finally, the [1,4] pathway takes

place in a very few cases where the steric factors are important or when the alkene is an allene or a diene. In the case of the unsubstituted reactants (benzene + ethylene), the wavelength of light used in experiments suggests that the reaction proceeds via the lowest-lying singlet excited state of benzene. In this case, the ratio of meta to ortho adduct is approximately 50:50. There are only a few theoretical discussions of this reaction, mainly based on orbital symmetry rules, frontier orbital theory and qualitative molecular orbital diagrams.

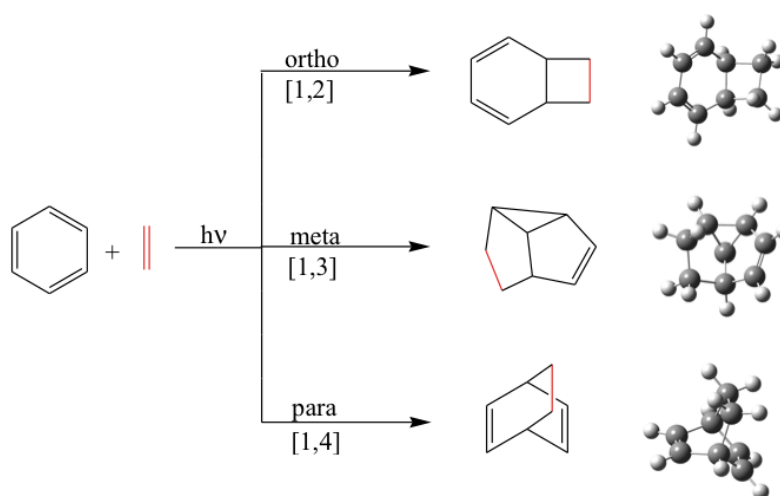


Figure 1. Photocycloaddition modes in benzene+ethene reaction. The C-C ethylenic bond is in red.

In this regard, it was necessary to analyse the role of the CI seam in such a photochemical reaction, with a reliable multiconfigurational method such as CASSCF. The main objectives of the project were to analyse the role of CI seams in photochemical processes. As one can see in the section “Research methodology” of the grant agreement, the original objectives of the project have been achieved, namely:

- (a) Mapping out the extended conical intersection seam :
1. Find critical points of conical intersection: minima and saddle points.
 2. Characterize these points using 2nd derivatives of the seam.
 3. Find pathways within the intersection space that link these points while still preserving the degeneracy.

(b) Mapping out adiabatic excited state reaction paths:

1. Understand the vibrational mode evolution along this path.
2. Determine which modes lead to the seam from along this optimised reaction path.

(c) How do the seams and pathways change when treating dynamic electron correlation? Comparing RASSCF vs. CASPT2 :

1. How to choose an extended orbital active space for RASSCF.
2. Compare RASSCF methodology with CASPT2 (energies)//CASSCF (geometries) methodology, in which the previous research of the fellow focused on to compute energies and to locate conical intersections along the PESs of biomolecules.

To achieve these goals we needed:

- 1) To explore and analyse the extended seam of geometries in the photocycloaddition ethene+ethene, in order to study different CI geometries at second order and to demonstrate if they belong to the same seam or not using VB theory, as well as analysing if some CI geometries in ethene+ethene were similar geometrically to benzene+ethene. This was a training exercise for the more complex benzene+ethene reaction.
- 2) To explore and analyse the extended seam of geometries in the photocycloaddition benzene+ethene, especially in order to understand the ratio of products (regioselectivity), analysing as well the accessibility of the seam from the S_1 excited-state hypersurface and the way to form ground-state products.
- 3) Understand the role of these seams theoretically with VB theory.

In addition, we faced some challenges in the study of the benzene+ethene system:

- i) Presence of a plethora of structures at S_1 PES, S_1/S_0 seam, and S_0 PES.

- ii) Presence of many biradical structures which are very difficult to deal with, since some parts of the supermolecule may present a barrierless rotation (then we can find multiple stationary points very close in energy). In addition, this fact may well lead to near-zero values of the Hessian matrix, which can give rise to problems in convergence.
- iii) The need of carrying out several minimum energy paths and/or steepest descent paths among the stationary points (sometimes using non-standard techniques) in order to confirm the connections. Actually, sometime it was very difficult to run MEP, due to convergence problems or because the starting point was a second-order saddle point and not a transition state, and then the SDP strategy was the only solution.
- iv) The presence of several possible pathways at similar energies.

As we stated in the grant agreement, these studies can be considered as a complementary step on the background of the fellow, taking into account his background during the PhD in Spain. With this knowledge, the fellow has developed skills to use high-level quantum-chemical packages such as Gaussian and Molcas, understanding the advantages and disadvantages of some methods and programs.

Results and Discussion

We have mapped the CI seam of two systems: ethene+ethene and benzene+ethene. In addition, some substituent effects on the latter are being investigated now. In both systems, CI structures have already been obtained in the past by researchers of this group (for the former, see Bernardi et al. Acc. Chem. Res. 1990, 93, 405; and for the latter see Clifford et al. J. Am. Chem. Soc. 1996, 118, 7353). However, with the new code developed here, it is now possible to analyse and understand better the role of the CI seam in photochemical reactions.

In ethene+ethene, as a training exercise, we studied the supra-supra, supra-antara, and antara-antara highest-symmetric CI, and we analysed the result using VB theory, with concepts which are very close to structural organic chemistry. On the other hand, in benzene+ethene we analysed exhaustively the S_1/S_0 seam as well as the accessibility of such CI structures and the multiple pathways to the three possible products.

Regarding the results, for ethene+ethene we demonstrated that all the CI lie on the same seam, and we analysed the geometries and branching space vectors with VB theory. For benzene+ethene we described three competitive paths from the reactants to the products (i.e. upon absorption of a photon, the paths from S_1 reactants to the seam, and from the seam to the S_0 products), as well as we analyse the topology of the seam with VB theory.

A) ETHENE+ETHENE

We will start with the main results of the ethene+ethene study. In this article we have looked at the photochemical 2+2 addition of two ethylene molecules from two complementary points of view: 1) a VB analysis of the seam of conical intersection for two 2-electron spin-coupled VB wavefunctions which we used to derive analytic exchange integral conditions and analytic branching space vectors; and 2) a numerical optimization of critical points on the intersection seam using CASSCF computations. The CASSCF wave function used to locate these crossing points includes all configurations generated by four electrons in four π MOs, with a 6-31G* basis set. All of the calculations were carried out using a development version of Gaussian 09 in which the new code developed by Sicilia et al. is implemented.

The conical intersection seam for the 2_s+2_s (face to face or supra-supra), 2_s+2_a (face to edge or supra-antara) and 2_a+2_a (edge to edge or antara-antara) cycloadditions of two ethylenes has been computed and the branching space vectors determined. The agreement between the analytic results from the VB analysis (which is the same for the 2_s+2_s , 2_s+2_a and 2_a+2_a) is good. This agreement suggests that the simple VB model is capable of rationalizing the general class of 2+2 cycloaddition reactions. The agreement of VB and numerical results shows that Woodward-Hoffmann symmetry forbidden and

allowed photochemical reactions are associated with the same conical intersection seam in this case.

In a previous paper (as it is stated before) the supra-supra photocycloaddition was studied in this group, and the CI corresponding to this process was optimized (supra-supra). Now in this paper, for the first time, we take into account the other two possible conformers: supra-antara and antara-antara. With the exception of the previously identified 2_s+2_s structure, which is the global minimum in the intersection space, the remaining optimized critical points are associated with multiple directions of negative (seam) curvature. While most of these negative directions of curvature point towards nearby conformational (i.e. torsional) “minima” on the seam (which still have other negative directions of curvature), there is always one direction that points towards the global 2_s+2_s crossing minimum.

In addition, a VB analysis was carried out. At a conical intersection the bonding situation of the excited state and the ground state matches perfectly so that the ground state and the excited state become degenerate. In general, the total energy of a system is, according to the London formula, $E = Q \pm K$, being Q the Coulomb integral and K the exchange integral. The coulomb contribution Q (which is the same for both ground and excited states) includes all the energy effects associated with the inactive orbitals and depends mainly upon the nonbonded repulsions and steric effects, whereas the exchange contribution K measures the bonding energy effects for the active electrons (i.e. those involved in bond making and breaking). Different points on the same conical intersection seam retain this balance and the energy difference between points on the same seam arises from Coulomb effects (e.g., steric effects). Hence two points on the same CI seam may have different energy for strictly steric reasons, but retaining the degeneracy between the two electronic states involved in such a crossing. Actually, if all the CIs lie on the same seam, then the difference among them will be due to the Q term only. Therefore it is possible to rationalize and predict the geometries and properties (specifically, the nature of the branching space) of conical intersections using valence-bond models, which can be useful to understand the origin of the topological features of the potential surfaces. In other words, analyzing the distances and overlap among the protagonist centres i and j (exchange integrals K_{ij}), it is possible to rationalize CI geometries.

Using such VB models, the condition for the four orbital-four electron (the model ethene+ethene) conical intersection can be derived. In addition, one can also predict the branching space vectors that lift the degeneracy. Specifically, the condition for the conical intersection in this system is:

$$K_{14} + K_{23} = K_{12} + K_{34} = K_{13} + K_{24}$$

being 1—2 and 3—4 the C atoms which are originally bonded forming two ethylenes. Then our aim is to obtain some CI structures and demonstrate that this relationships is fulfilled in all of them.

Following the objectives listed in the previous section (specifically a.1 and a.2), we have characterized some CI structures at second order (see Figure 2). The 2_s+2_a structure (130 kcal mol⁻¹ above the 2_s+2_s structure) has C_{2v} symmetry with 4 imaginary frequencies, while the D_{2h} 2_a+2_a structure (212 kcal mol⁻¹ above the 2_s+2_s) has 6 imaginary frequencies. In both cases, we have been able to optimize lower-symmetry structures that are closely related by displacing along some of these negative directions of curvature. However, these structures are still high in energy with negative directions of curvature remaining. Since our main objective is to compare analytic VB and calculated CASSCF results, we shall ignore these closely-related structures, and discuss only the highest-symmetry structures explicitly here.

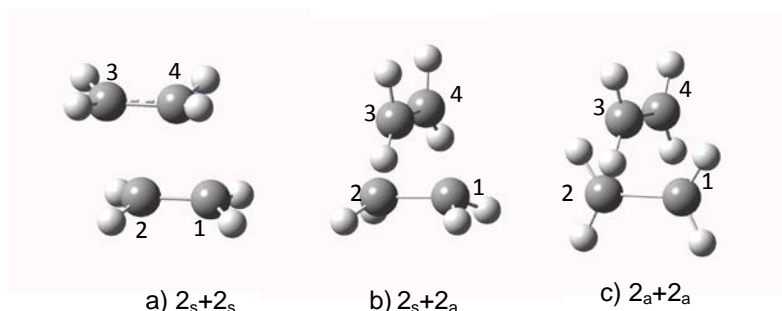


Figure 2. (a) Supra-supra, (b) supra-antara and (c) antara-antara conical intersections found in the ethylene+ethylene system.

In each case, the identities in the previous equation are satisfied approximately, and then we can conclude that all three CI lie on the same seam and conform to the same VB model. It is possible to illustrate as well the agreement between the VB model and the

BS vectors calculated at CASSCF level, as it is fully explained in the corresponding paper.

B) BENZENE+ETHENE

Now we shall move on to the benzene+ethene reaction. All the electronic structure calculations (optimizations, MEPs, etc...) were carried out using the CASSCF (8,8) method, with a 6-31G* basis set, with a development version of Gaussian09 in which the new code developed by Sicilia et al. is implemented. For some points we have analysed the effect of dynamic electron correlation on excited state energies with the CASPT2 method, using the program MOLCAS-7.

As we have stated in previous section, we have carried out a full second order analysis of critical points on the conical intersection seam, and then we could perform frequency analysis of vibrations confined to the seam and optimize minima and transition states within the space of the seam. We could also compute minimum energy paths from a first-order saddle point (transition state, TS) on the seam (which we shall refer to as a seam-MEP) and thus map out a segment of the seam.

Besides this, reaction pathways from transition states on the S_1 PES were characterized in forward and reverse direction by an intrinsic reaction coordinate (IRC) analysis finding the MEP (in this case the MEP was carried out in the full space). On the products side, the determination of possible reaction paths on the ground state from a CI point required a different strategy. There is no unique initial search vector (such as the transition vector at a TS), so one must test several possibilities. In general one can choose either i) one of the branching space vectors, ii) the gradient of one of the degenerate states (neither of the two gradients is null at a CI geometry, in contrast with “standard” stationary points), or iii) a vector connecting the CI geometry and some other structure such as a product. In some cases the preceding strategy is awkward due to convergence problems because there is a “downward direction” but no “valley”. In that case we used a steepest descent path (SDP): from a given point, one follows the gradient vector (without mass-weighting) in the downhill direction with a fixed identity

hessian matrix. Thus, if the step size is sufficiently small, this procedure will terminate at the “closest” critical point. Just like an MEP from a CI, one must choose a search vector (specifically the gradients of both hypersurfaces at the crossing point) and an initial geometry along this direction. Of course, in cases where both MEP and SDP were possible, the end point was the same.

We also wish to understand the electronic origin of the conical intersection seam in terms of VB structures (a possible way of drawing classical chemical bonds in order to accommodate all the electrons from a set of singly occupied valence orbitals). To obtain this information, we have performed a VB analysis of the ground and excited state wavefunctions at points on the conical intersection seam. This analysis was carried out by computing the VB wavefunctions using the MMVB method and, in some cases, performing an analysis of spin exchange density matrix obtained with CASSCF. The numerical results were similar with both methods.

The main results are summarized in the following figures (see Figures 3-5):

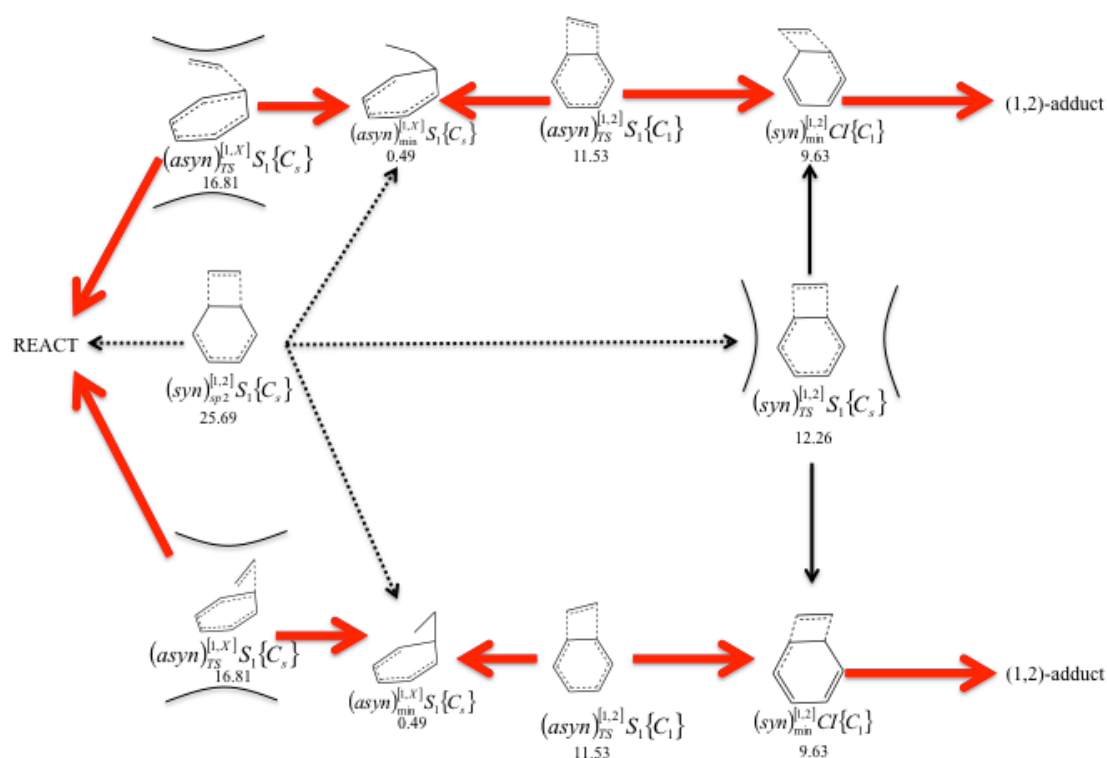


Figure 3. Schematic map of the important critical points associated with the 1,2 regioselectivity of ethylene + benzene on S_1 . Energies relative to the S_1 state of benzene + ethylene (S_0) in kcal mol⁻¹. Solid arrows indicate MEP dashed arrows indicate SDP. The highlighted red arrows indicate the mixed asynchronous/synchronous [1,2] path: ASYN1X-S1-TS, ASYN1X-S1-min, ASYN12-S1-TS, to SYN12-CI-min.

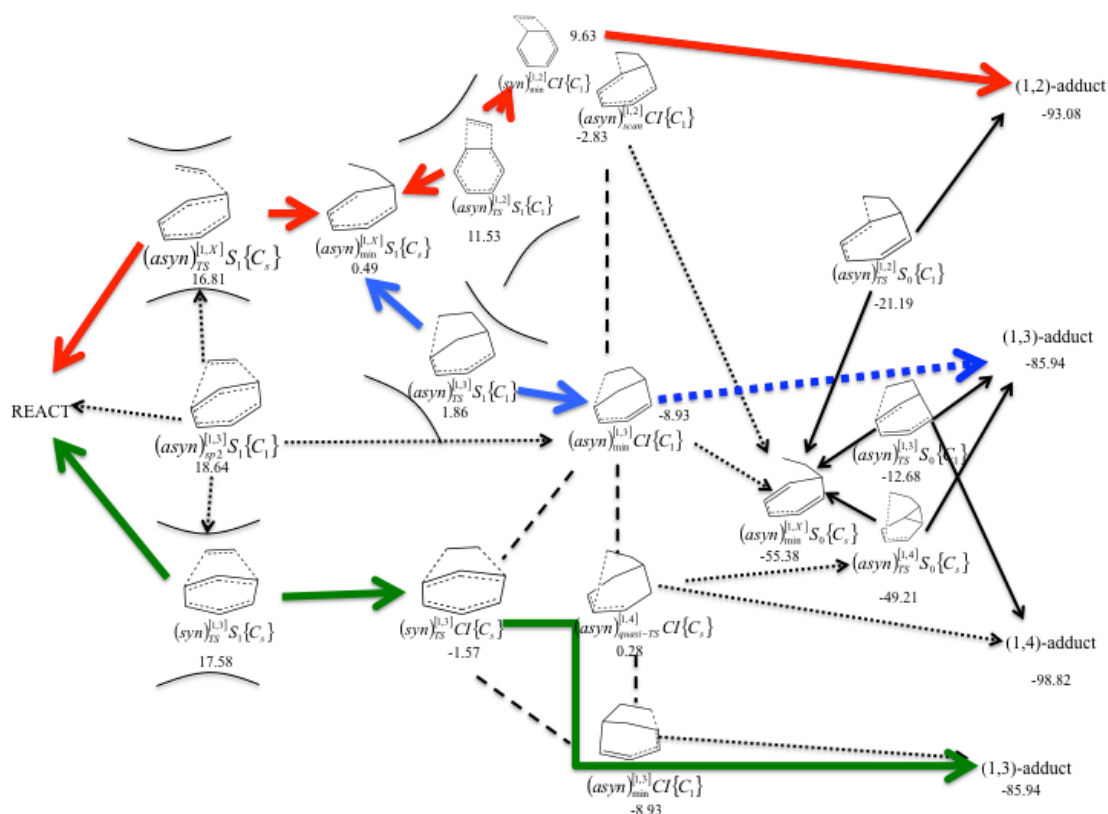


Figure 4. Schematic map of the important critical points associated with the (1,2)-(1,3) regioselectivity. The topology of the surface around the various TS is indicated with the pairs of concave lines. Energies are S_1 state of benzene + ethylene (S_0) in kcal mol⁻¹. Dashed lines mean paths within the seam. The highlighted paths (colored) correspond to: red, the mixed asynchronous/synchronous [1,2] path: ASYN1X-S1-TS, ASYN1X-S1-min, ASYN12-S1-TS, to SYN12-CI-min; the asynchronous [1,3] path: ASYN1X-S1-TS, ASYN1X-S1-MIN, ASYN13-S1-TS and ASYN13-CI-min; and synchronous [1,3] path: from SYN13-S1-TS to SYN13-CI-TS.

Bear in mind that the notation in the figures displays more information than that of within the text, but the link is easy to follow in all the cases. We have used a different notation in the text for the sake of simplicity.

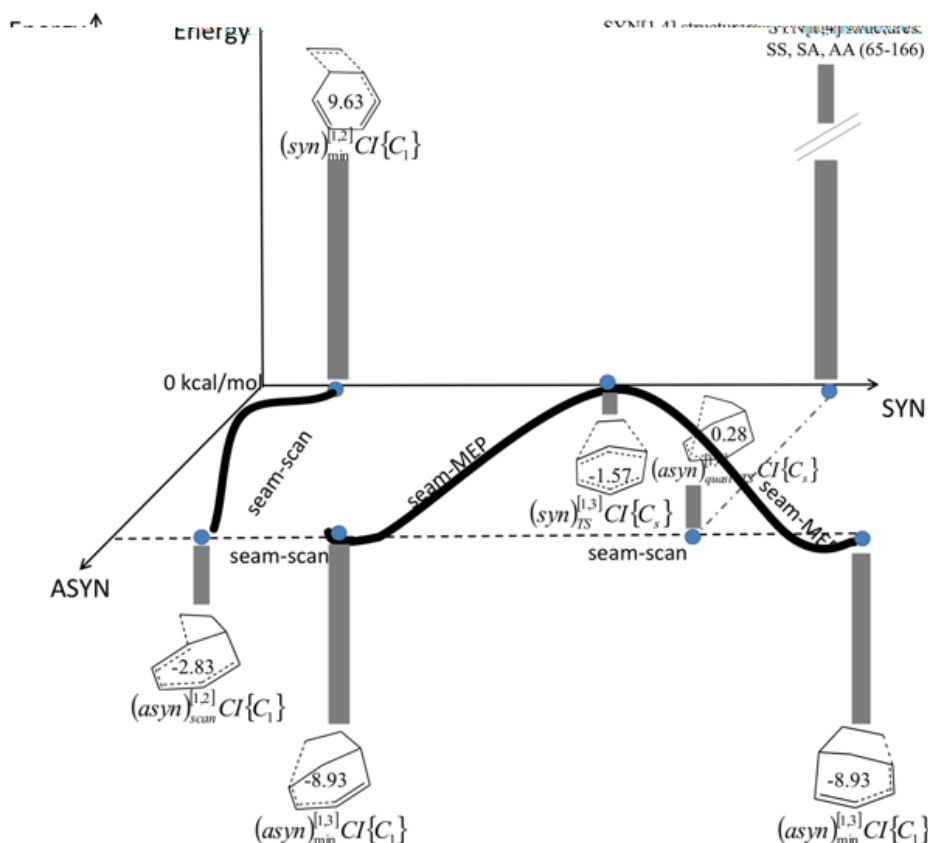


Figure 5. Energies and connectivity of points on the conical intersection seam for the asynchronous (ASYN y axis) and the synchronous (SYN x axis) approach. The connectivity (solid heavy lines) is either by a seam-MEP (ie reaction path constrained to lie within the seam) or a seam-scan (where the torsional co-ordinate is selected as a distinguished variable and the CI point is optimized under constraint) Energies relative to S_1 state of benzene + ethylene (S_0) in kcal mol⁻¹.

In all the important regions (S_1 on reactant side, S_1/S_0 seam and S_0 on product side) we have found structures which are *ortho* (1,2), *meta* (1,3) and *para* (1,4), and others which cannot be ascribed to any of them, which are *biradical* structures (1,X), where we use this notation to indicate an open biradical structure with no secondary C-C σ bond. In addition, in discussing the possible paths, we are going to highlight those mechanisms in which we can draw a path from reactants to the seam, and to the seam to products, *involving only minima and transition states*. Any other path containing higher-order saddle points cannot be crucial in the photochemical transformation. For instance, a second-order saddle point (SP2) has two directions of negative curvature (imaginary frequencies): one of these directions may correspond to a reaction pathway while the other may connect two different paths. Therefore a second-order saddle point is a mountain top locally and no reaction path would contain such a point; rather, such a point separates two possible reaction pathways containing transition states.

In general, there are then 3 main steps associated with a photochemical path from reactants to products. The first step involves the reaction path from the reactants to the conical intersection seam, possibly involving a transition state (which is necessary to overcome) and/or intermediates (local minima). The second step involves radiationless decay at the conical intersection seam itself. Finally, the third step involves the reaction paths that become possible via the decay at the conical intersection. However, the CI seam is a sieve from reactants to products, since only the accessible (both energetically and conformationally) CI are important mechanistically. From the previous figures it can be seen that there are two overlapping “active” mechanistic pathways corresponding to transition states between the reactants and the conical intersection seam. This topology yields three reaction paths:

- i) a mixed asynchronous/synchronous [1,2] path: ASYN1X-S1-TS, ASYN1X-S1-min, ASYN12-S1-TS, to SYN12-CI-min
- ii) an asynchronous [1,3] path: ASYN1X-S1-TS, ASYN1X-S1-MIN, ASYN13-S1-TS and finally ASYN13-CI-min
- iii) a synchronous [1,3] path: SYN13-S1-TS to SYN13-CI-TS

We are going to analyse the mechanism in further detail. There are two important transition states on the S_1 PES: ASYN1X-S1-TS and SYN13-S1-TS, which form the dynamical bottleneck on the path to the conical intersection seam. These two structures, which form the barrier between the reactants and the CI seam or the intermediate (local minima on the S_1 PES), are very close in energy. We have also carried out CASPT2 computations on these three structures in order to take into account dynamic correlation effects in computing energies. In both cases, the activation energy becomes negative (i.e. the energy is below S_1 benzene + ethylene at 10 Å). This clearly indicates the need to re-optimize the geometries at the CASPT2 (which is not feasible technically) or RASSCF level (which is very time-consuming). But it also suggests that the barrier heights might be quite small and this could be consistent with the fact that no wavelength-dependence is observed experimentally. Thus the important point is that these transition states serve mainly to restrict the spread of the wavepacket (dynamical

bottleneck) directing it towards the seam (i.e. transition state theory that assumes thermal equilibrium between the TS and reactants is not applicable).

We now begin a discussion of the main features of the S_1 [1,2] reaction pathway (see Figure 3). The potential energy surface for the synchronous [1,2] pathway is very similar to that for classic ethylene + ethylene discussed in the previous system. There are two CI points equivalent by symmetry denoted SYN12-CI-min (equivalent to the supra-supra CI on ethene+ethene) interconnected by a transition state on S_1 , SYN12-S1-TS. However, there is no “real” synchronous [1,2] pathway from reactants: instead of a transition state along a C_s reaction path, one finds a point with two imaginary frequencies (a local mountain top), denoted SYN12-S1-SP2. The extra negative direction of curvature leads to the two equivalent lower energy asynchronous biradical pathways, passing via a biradical intermediate ASYN1X-S1-TS.

Now we turn to the synchronous [1,3] pathway and the asynchronous biradical pathways (see Figure 4). These two pathways have the initial transition states SYN13-S1-TS and ASYN1X-S1-TS. These pathways are separated by a second-order saddle point, denoted as SYN12-S1-SP2. Surmounting the biradical TS, we find a biradical minimum, ASYN1X-S1-min. From this biradical intermediate, there are 2 active reaction paths to the seam via S_1 transition states: 1) via ASYN12-S1-TS leading to SYN12-CI-min, that we have just discussed; and 2) via ASYN13-S1-TS leading to ASYN13-CI-min. A [1,4] path is also possible in theory. However, we were unable to optimize a true transition state. Beginning at the maximum of a linear interpolation path between ASYN1X-S1-min and ASYN14-CI-TS, we found only an “orthogonal” TS connecting two equivalent [1,3] pathways. Thus the 1,4 path appears to be located on a ridge between asynchronous 1,3 approaches.

There remains the question about whether there is a possible [1,2] path via the biradical intermediate ASYN1X-S1-MIN that does not pass via ASYN12-S1-TS but rather leads to the asynchronous part of the conical intersection seam. A linear interpolation between ASYN1X-S1-min and the point ASYN12-CI-scan on the seam passed through a maximum at 14.01 kcal mol⁻¹. However, we were not able to find a true transition state. Thus it is most likely that the [1,2] transition structure lies on the “side” of the [1,3] asynchronous valley.

Our discussion will now be focused on the conceptual aspects of the conical intersection seam (see Figure 5). We begin with a discussion of the asynchronous conical intersection seam, comprising the optimized asynchronous critical points ASYN12-CI-scan, ASYN13-CI-min and ASYN14-CI-TS. The additional point ASYN12-CI-scan (we could not find a critical point in this region) was obtained by a torsional coordinate constrained conical intersection optimization (i.e. seam-scan). The maximum on the seam ASYN14-CI-TS is only a very shallow local minimum (then it is more suitable the notation *quasi-TS*). An [1,4] asynchronous S_1 path passes along a ridge on S_1 , separating the two symmetry equivalent versions of ASYN13-CI-min. It is clear that such a point is the lowest energy point on the seam. The other two asynchronous CI lie higher in energy and there may be less important, since one can expect radiationless decay to occur near minima on the seam rather than maxima. On the other hand, the synchronous structure named SYN12-CI-min is much higher in energy than the asynchronous seam points. Further, while SYN13-CI-TS has a lower energy, it is a saddle point on the seam; and it can be interpreted in the same way as ASYN14-CI-TS in the asynchronous path (another “maximum” on the seam).

In addition, it was possible to carry out a seam-scan connecting ASYN12-CI-scan and SYN12-CI-min, as well as a seam-MEP connecting SYN13-CI-TS and ASYN13-CI-min, then fulfilling points a.1, a.2 and a.3 of the objectives displayed in the previous section). This fact is important mechanistically, pointing out that all the CI points lie on the same branch of the seam (remember that all the asynchronous CI are in fact connected through a seam-scan). This statement was already true in ethene+ethene, but in this case the picture is more complicated than the 4-electron-4-orbital model, which could be derived analytically in that case.

It now remains to briefly discuss the final phase of the reaction paths; namely, from the conical intersection seam to products on S_0 . To document such paths one might use quantum dynamics. Here we have chosen (for many examples) to simply follow a path of steepest descent (SDP), following the gradient vector with small step sizes. In some cases the ground state reaction path is clear. For example, SYN13-CI-TS has an SDP that terminates directly at a [1,3] adduct and an SDP that goes back to the ground state reactants (characteristic of a “peaked” conical intersection). The situation for the asynchronous pathways from the conical intersection is less clear. On the one hand, we

can find an SDP from ASYN13-CI-min to a 1,3 adduct. On the other hand, there is a backward SDP that terminates at a ground state biradical minimum ASYN1X-S0-min.

To summarize, in the photocycloaddition of an arene and an alkene there are 3 possible regioselectivities: ortho (1,2), meta (1,3) and para (1,4). In this work we show that this regioselectivity is, in part, controlled by an extended conical intersection seam and that the shape of the conical intersection seam can be understood in terms of simple VB arguments. Of course, access to the conical intersection seam is in turn determined by the shape of the S_1 potential surface. It is important to highlight that, as one can read in the previous section (specifically points b.1 and b.2), we have analyzed the vibrational modes which link different structures within the mechanism: ASYN1X-TS may connect the reactants and ASYN1X-MIN, ASYN12-TS may connect ASYN1X-MIN and SYN12-CI, ASYN13-TS may connect ASYN1X-MIN and ASYN13-CI, and SYN13-TS may connect reactants and SYN13-CI. From the S_1 PES the seam is reached (ASYN12-TS will lead to SYN12-CI, ASYN13-TS will lead to ASYN13-CI, and SYN13-TS will lead to SYN13-CI) in a barrierless way.

As one can see in the following and simplified scheme (see Figure 6), there are two TS which control the access to the seam: ASYN1X-TS and SYN13-TS. If the system evolves through the latter, then we reach the seam directly (SYN13-CI). On the contrary, if the former is followed, we reached an intermediate (ASYN1X-MIN), and two new barriers may be overcome, ASYN12-TS and ASYN13-TS, before reaching the S_1/S_0 seam (to form SYN12-CI or ASYN13-CI, respectively). Then we have a first comparison to do: ASYN1X-TS vs. SYN13-TS, and if ASYN1X-TS is more favorable, we have to do a second comparison: ASYN12-TS vs. ASYN13-TS

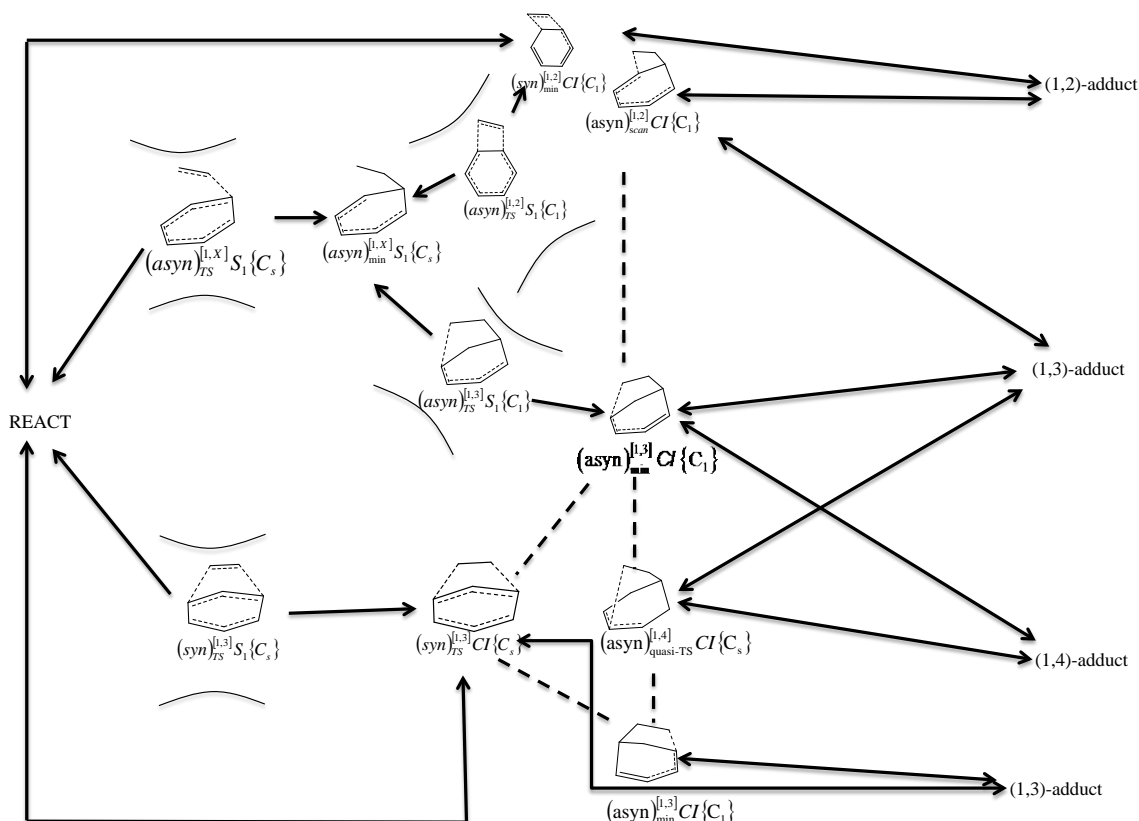


Figure 6. Simplified scheme of the benzene+ethene reaction.

If one ignores any structures on S_1 for the moment, then the shape and energetics of the asynchronous conical intersection seam, suggests that 1,2 and 1,3 will be the preferred regioselectivities with similar weight. The syn 1,4 regioselectivity seems impossible on the basis of energetics and the asynchronous 1,4 path is associated with a maximum on the seam. The 1,3 asynchronous structure ASYN13-CI-min is the lowest point on the S_1 potential surface with ASYN12-CI-scan slightly higher. Thus there exists an extended low energy region of the conical intersection seam centred on ASYN13-CI-min. VB analysis shows that the pairs of VB structures along this asynchronous seam are the same and thus the shape will be determined mainly by steric effects. The synchronous [1,2] conical intersection point is much higher in energy.

Finally, substituent effects are being studied currently, with benzene and substituted alkenes: tetrafluoroethylene (as an example of a system with electron-withdrawing groups), 2,3-dimethyl-2-butene (as an example of a system with electron-donating groups), and fluoroethene (AKA vinyl fluoride, as an example of an asymmetrically

substituted ethylene). As we have just stated, this study is currently in progress and only preliminary conclusions can be displayed.

Among all the points which are already optimized, the asynchronous ASYN13-CI is the lowest-lying point on S_1 PES. In addition, the normal modes associated to the imaginary frequencies of the transition states and the branching space vectors of the CI points are essentially the same as in benzene+ethene. Again, all the CI points are peaked and from the S_1 PES the seam is reached in a barrierless way. To summarize:

- a) Benzene+ethene: the gap between ASYN1X-TS and SYN13-TS is just 0.77 kcal/mol, then both paths are likely to happen. However, if ASYN1X-TS is followed, then ASYN13-TS is much lower in energy than ASYN12-TS (1.37 vs. 11.04 kcal/mol, taking into account the gap with the biradical minimum ASYN1X-MIN), then favoring the formation of the meta CI.
- b) Benzene+tetrafluoroethene: now the gap between ASYN1X-TS and SYN13-TS is 10.87 kcal/mol, then favouring clearly the path through the biradical transition state, ruling out the path through SYN13-TS. Once the biradical minimum is reached, the barriers to ASYN12-TS and ASYN13-TS are 27.14 and 1.79 kcal/mol, respectively, then favoring clearly ASYN13-TS and the formation of the meta conical intersection. In addition, the dipole moments of the asynchronous structures (ASYN12-TS and ASYN13-TS) are ca. 1.5 D higher than that of the rest, then in polar solvents they will be stabilized (spectral red-shift).
- c) Benzene+2,3-dimethyl-2-butene: ASYN1X-TS is 2.06 kcal/mol lower in energy than SYN13-TS, then in this case the path which involves SYN13-TS is slightly more unlikely than in (a). Following the more likely path, the barriers are 6.85 kcal/mol and -0.05 kcal/mol (ASYN13-TS is even lower in energy). Therefore in this case the formation of ASYN13-TS is barrierless and even more favorable than in (a).
- d) Benzene+fluoroethene: in this case (example with an “asymmetric” ethylene) we are still looking for SYN12-CI and SYN13-CI. However, we have already enough points to analyze the accessibility to the seam. In this case, ASYN1X-TS is a bit lower in energy than the reference (-1.43 kcal/mol) and more favorable

than SYN13-TS (1.88 kcal/mol; there the two distances are now slightly different, but it is still a synchronous structure). However, the difference is not as huge as in (b), then adding more fluorine atoms makes the biradical/asynchronous path more favorable than the synchronous one. Next, the gap with respect to the biradical minimum is 3.19 kcal/mol (ASYN13-TS) and 14.47 kcal/mol (ASYN12-TS), therefore again the ASYN13 path is more likely to take place. Again, with 4 F atoms (case (b)) this difference was even larger. Finally, the point ASYN14-CI was obtained with a dihedral frozen, since the (1,3) CI is formed if the constrain is removed.

Potential impact and dissemination activities

Photochemistry is a very important discipline with a plethora of applications. Life on Earth depends, both directly and indirectly, on the influence that light has on chemistry. Indeed, the interaction between radiation and matter is important at different levels. Interaction of light with tissues or, in general, living or non-living entities, is a complex phenomenon which lies on the borders among Physics, Chemistry and Biology and lead to many developments: understanding the effects of electromagnetic radiation on living tissues (DNA alteration, phototherapy...), designing light harvesting systems for clean and sustainable energy generation, photocatalysis and the design of efficient light-driven molecular devices for data storage and processing, photoactive materials with particular chemical, biological, energy or information storage properties. Understanding spectroscopic phenomena at molecular level will provide meaningful information that may well be the source of interesting advances. If we can learn to design molecules that interact with light predictably, we will provide an essential knowledge on the development of chemical engineering, nanotechnology, materials science or photobiology. Therefore any study that explains the role of CIs may well be importance to develop coherence control and femtochemistry, in order to analyse chemical transformations which take place on extremely short timescales.

This is the first time in which two actual photochemical systems (ethene+ethene, and benzene+ethene) have been studied up to second order using the method developed by Sicilia et al. at CASSCF level of theory, characterizing and mapping the S_1/S_0 seam. Cycloadditions with alkenes are important and characteristic photochemical reactions of aromatic compounds. It was difficult how to rationalize the ratio of products (ortho:meta:para), as well as the role of the S_1/S_0 seam. The understanding of the role of the seams in photochemical reactions may well be priceless to understand many experimental results and to put forward better synthetic routes to obtain interesting chemical products.

In essence, the aim of mapping the seam is to understand its nature and the connection among the points, as well as to identify all the possible decay paths from the seam to products, which may give rise to different photoproducts, including those that are formed at high excitation energies. Actually, the competition between the products may well depend on where the seam is accessed after the initial excitation and after surmounting the barriers along the S_1 PES. In other words, the lowest-lying CI may not be the most important one, but the one which is more accessible. Besides this, there may be points on the seam which are not relevant photochemically. In this regard, the seam can be considered as a *sieve* from the S_1 PES on the reactant side to the S_0 PES on the product side, and then it is important to characterize CI geometries exhaustively. On the other hand, taken into account that this has been a static study (i.e. we have not carried out dynamics calculations to understand the propagation of wavepackets), we have not taken into account the vibrational excess energy, and the system may follow any of the found pathways since the energy differences are not huge. We have to bear in mind that a picture of the dynamics of this system may well be important to confirm the preferential path, since the study of the wavepacket propagation gives some aspects which cannot be deduced from the static picture provided here analyzing the potential energy hypersurfaces

The dissemination activities spanned 3 international conferences which were focused on photochemistry and non-adiabatic processes, as it is displayed in a following section. In addition, apart from the dissemination activities, the results and knowledge from this project have been very useful in the study of the dynamics of cyclohexadiene, carried

out together with other members of the group, as well as the teaching duties of the fellow, since he has been one of the teachers of an international master school celebrated in 2011 and 2012:

EUROPEAN SCHOOL ON THE DYNAMICS OF MOLECULAR EXCITED STATES INDUCED BY ULTRASHORT PULSES. M1 Excited States. COST

Action CM0702. Erasmus Mundus Master Course in Theoretical Chemistry and Computational Modelling (TCCM). Course 2010/11. Zaragoza Scientific Centre for Advanced Modeling ZCAM.

TCCM European School on Molecular Excited States . Basic Concepts in Modern Molecular Photochemistry. Erasmus Mundus Master Course in Theoretical Chemistry and Computational Modelling (TCCM). Course 2011/12. Zaragoza Scientific Centre for Advanced Modeling ZCAM.