However, this paper presents a rationalization which suggests that $Fe(CO)_4$ with its IR laser induced isomerization is a unique manifestation of the Jahn–Teller effect. Moreover, our topological model, the *distortion octahedron*, which was developed to study the pseudorotation, should be more generally applicable to the distortions of other four-coordinate molecules.

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Fragments in Molecules: The Decomposition of Reaction Surfaces into Diabatic Components in the Framework of an ab Initio CI Approach

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Abstract: In the present paper we describe a procedure for the computation of diabatic surfaces, defined in the framework of an ab initio CI approach. The main feature of this procedure is that each diabatic surface is associated with a specific bonding situation and thus with a specific packet of configurations built from the valence orbitals of the fragments. This computational procedure is applied here for illustrative purposes to some reactivity problems, such as the cyanate–isocyanate rearrangement, the [1,2]-sigmatropic shift in propene, a model S_N2 reaction, and the addition of singlet methylene to ethylene. It is shown that in each case this type of quantitative analysis provides a clear understanding of the origin of the various transition states occurring in these reactions.

1. Introduction

The analysis of adiabatic surfaces in terms of diabatic components is playing an increasingly important role in the interpretation of organic phenomena.[2-4] Two quantum mechanical formalisms have been essentially used for such analyses; one is related to the molecular orbital (MO) method[2,5] and the other, the LCFC (linear combination of fragment configurations) approach,[3,4] is related to the valence bond (VB) method, and both have been essentially applied at a qualitative level.

During the past 5 years there have been important technical advances in the quantum mechanical methods available for the computation of molecular potential energy surfaces, and the ab initio optimization of geometries of equilibrium and transition states is now practical.[6] We have now reached the point where it is necessary to analyze these surfaces in a quantitative way. The central problem in implementing such a computational procedure in a quantitative fashion is the formulation of a precise operational quantum mechanical definition of the diabatic surfaces themselves. In the MO method, where the orbitals are the MO's of the molecular problem under investigation, the diabatic surfaces are associated with the various MO configurations; while in the LCFC approach, where the orbitals are those of the molecular fragments or reactants, the diabatic surfaces are associated with the isolated fragment, charge transfer, and locally excited configurations. The two formalisms can be interconnected in both a qualitative and quantitative manner[7] and in the limit yield the same adiabatic surface. However, the decomposition into diabatic curves may be very different in the two models.

In the present work we shall use a LCFC formalism, with the definition that each diabatic surface describes a specific bonding situation in terms of the orbitals of the isolated fragments. This definition will lead to clearly defined diabatic surfaces and related crossings in the various kinds of reactivity problems.

In this paper we describe first a quantitative procedure based on a CI approach for computing these diabatic surfaces. All computations presented here have been performed at the STO-3G level[8] using the for the integral evaluation and the solution of the SCF equations the GAUSSIAN80 series of programs.[9] The matrix elements for the CI calculations have been computed by using the unitary group method described by Hegarty and Robb.[10]

While the quantitative procedure presented here can be applied in any atomic orbital basis, it is expected that already with a minimal basis set useful information can be obtained about the behavior of the various diabatic curves and the regions of crossings. This procedure can be used either for rationalizing the results of more sophisticated calculations or for obtaining information about

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[1] (a) Università di Bologna. (b) Queen Elizabeth College. Senior CIBA-GEIGY Fellow at the University of Bologna Jan 1–August 31, 1982.

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the regions of crossings to be investigated in greater detail. Here we apply such a procedure to analyze a variety of chemical problems to illustrate the possibilities of this type of quantitative analysis.

2. Ab Initio Computation of Diabatic Surfaces for Molecular Reactions.

Let us consider the reaction

$$X \rightleftharpoons Y \tag{1}$$

and let us assume that the associated adiabatic surface can be described in terms of two variables R_x and R_y (these could be the distances of the incoming and leaving groups in an S_N2 reaction, for example). We assume also that we can model the reaction surface with two diabatic surfaces $E_x(R_x,R_y)$ and $E_y(R_x,R_y)$. The surface $E_x(R_x,R_y)$ describes the "bonding situation" appropriate to the species X at all regions of the configuration space (including the region of the minimum of the surface E_y). Further, the adiabatic surface should be represented almost exactly by $E_X(R_x,R_y)$ in the region of its minimum.

In translating this model into quantum chemistry, the problem reduces to formulating a definition for the wave function corresponding to $E_x(R_x,R_y)$ that describes the "bonding situation" at X for all regions of the configuration space. Alternatively, the wave function corresponding to $E_x(R_x,R_y)$ must explicitly exclude the "bonding situation" corresponding to $E_y(R_x,R_y)$. Obviously a similar line of reasoning holds for the other diabatic surface $E_y(R_x,R_y)$. We now proceed to formulate such definitions.

Let us assume that the wave function for the adiabatic surface can be represented by a CI expansion,

$$\Psi = \sum_k c_k \Phi_k \tag{2}$$

for all values of the reaction coordinates R_x and R_y. The Φ_k are configuration state functions built from the orbitals of some noninteracting fragments, which could be chosen by setting R_x to ∞, R_y to ∞, or both.

It will be convenient to distinguish three types of orbitals:[11] (i) core orbitals which are doubly occupied in all configurations, (ii) valence (or active) orbitals which have all possible occupancies in the Φ_k, and (iii) virtual orbitals which are unoccupied in all configurations. In general the valence orbitals will correspond to those orbitals involved in bond making and bond breaking. We can distinguish two types of configurations: configurations corresponding to antisymmetrized products of isolated fragment configurations (IFC) and charge-transfer configurations (CTC) corresponding to electron transfer between fragments. The IFC include Heitler-London type configurations (HLC), which involve spin-paired open-shell fragments, and no-bond configurations (NBC), which refer to closed-shell configurations of the fragments (in ref 12 we have referred to both HLC and NBC as NBC). At infinite interfragment distance the IFC and CTC do not mix; however, at finite interfragment distance, their mixing is essential for a proper description of bonding. In general the spectroscopic states of the fragments will correspond to linear combinations of IFC; however, in many cases a given spectroscopic state will be dominated by a single IFC.

With these definitions at hand we can now define a model wave function corresponding to a diabatic surface. The model will involve three elements: (i) specification of the fragments, (ii) choice of the valence orbitals, and (iii) specification of a subset of IFC and CTC configurations built from the valence orbitals of the fragments that defines a "specific bonding situation" and hence a diabatic surface. When we come to the applications, the choice of the fragments is more or less obvious, the only condition is that the fragments have to be chosen so that the orbitals retain their character along the reaction coordinate. Also the choice of the valence orbitals is more or less obvious, since they are the fragment orbitals involved in the processes of bond making or breaking under examination. On the other hand the choice of the subset of IFC and CTC configurations that define a diabatic surface requires a more detailed discussion. In general we can identify a "bonding situation" with a combination of IFC (including all possible spin couplings for a given orbital occupancy). Thus we associate a bonding situation with a subset of configurations that correlate with given spectroscopic states of the fragments. In order to describe this "bonding situation" at a finite interfragment separation we must add charge-transfer configurations subject to the constraint that we explicitly exclude any IFC that describes a different "bonding situation". The latter constraint is relevant only if we have more than two fragments. In this case one IFC could be generated from another by charge transfer. Thus a diabatic surface is constructed from a wave function that contains a subset of IFC and CTC that describes a "specific bonding situation" and explicitly excludes others.

The practical implementation of the above ideas is described fully elsewhere;[12] however, for completeness, we summarize the main points here. The fragment orbitals are obtained by performing an MC-SCF computation at infinite interfragment separation. These orbitals are then orthogonalized at the particular interfragment distance of interest and the energies of the diabatic and adiabatic surfaces computed by CI. The effect of orbital mixing with core and virtual orbitals (orbital polarization and charge transfer) is computed by second-order perturbation theory or MC-SCF.

As discussed in some detail in ref 12, with this procedure the contribution of CTC relative to IFC will be larger than in a traditional VB calculation. This feature has no significant effects upon the energy profiles of the various adiabatic and diabatic surfaces. In fact these energy profiles contain the energy contributions from the IFC and CTC as well as those from orbital polarization and orbital charge transfer. The latter energy effects will counterbalance the overemphasis of the CTC with the result that the energy (diabatic or adiabatic) will be numerically equivalent to that obtained with a nonorthogonal VB procedure. However, the result of the effects of orbital polarization and orbital charge transfer on the wave functions itself (i.e., the changes in the CI expansion coefficients) is never computed and therefore it would be incorrect to assign too much significance to the expansion coefficients of the CTC and IFC themselves.

Finally, we should mention that in constructing the sets of configurations corresponding to a diabatic state we consider only the one-electron CTC derived from a IFC. The contribution of more than one-electron CTC is included in the adiabatic energy profiles and will be very large, for example, at the product geometry of an addition reaction, but will still be quite small in the region of the transition state itself.[12]

3. Applications

In this section we analyze a certain number of reactivity problems with the purpose of illustrating the origin of the various critical points that can be found in the energy profile.

3.1. Hydrogen Migration over a π Bond. As a first example of hydrogen migration along a π bond, we consider the rearrangement:

$$\text{H—CN} \rightarrow \text{CN—H} \tag{3}$$

The reaction coordinate for this rearrangement has been determined by Morokuma et al.[13] at the STO-3G level using SCF methods. The reaction profile shows only one transition state, with a barrier of 69.2 kcal/mol at the STO-3G level. The reaction path has a circular form at the beginning and at the end and in between proceeds more or less parallel to the CN bond.

For the computation of the diabatic surfaces the fragment decomposition is obvious; one should be able to describe the reaction in terms of configurations built from the CN fragment and the H atom. The ground state of the CN radical is a $^2\Sigma^+$ state with the odd electron in a σ orbital associated with the carbon atom (σ_C). There is also a low-lying doubly degenerate excited

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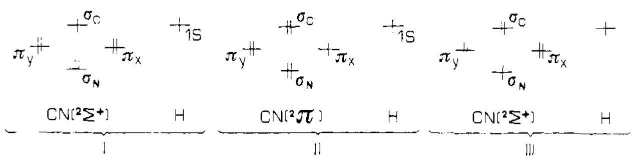

Figure 1. IFC involved in the rearrangement HCN → CNH.

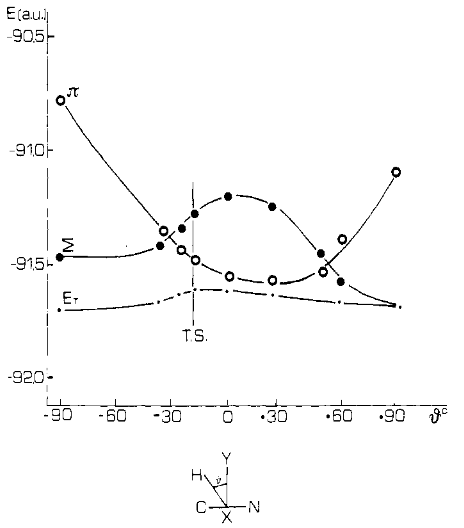

Figure 2. Diabatic curves (Π denotes the curve associated with the CN $^2\Pi$ IFC and Σ that associated with the two $^2\Sigma^+$ IFC) and total energy curve (E_T) for the rearrangement HCN → CNH.

state of CN, a $^2\Pi$ state, with the odd electron in a π orbital and a high-lying excited state of $^2\Sigma^+$ symmetry with the odd electron localized on the nitrogen atom (σ_N). The associated IFC are shown in Figure 1. Thus for this problem we should be able to describe the diabatic surfaces with five valence orbitals (two σ orbitals and two π orbitals of CN and the H 1s orbital), eight valence electrons, and a total of 15 configurations (of which only 11 have A' symmetry). The two diabatic surfaces will then correspond to the two $^2\Sigma^+$ IFC plus CTC for reactants and products and the two $^2\Pi$ IFC plus CTC for the transition structure.

The behavior of these diabatic surfaces along the reaction coordinate is illustrated in Figure 2 along with the 15-configuration MC-SCF result. The C–N distance in all these computations has been fixed at 1.22 Å (the value at the transition structure), and the H atom coordinate is represented in terms of the angle HXY, where X is the centroid of nuclear charge for the CN fragment. The points at 90° correspond to reactants and products and the transition state occurs at $\angle HXY \simeq 20°$. These results show that in the region of 0° the diabatic surface associated with the CN $^2\Pi$ IFC has a minimum while the $^2\Sigma^+$ surface has a maximum. They show also that there are two intersections, one on either side of the 0° point; however, these two intersections lead to a single transition state rather than two separated by a minimum. This behavior is due to the fact that the two diabatic surfaces interact strongly, and in these cases an intersection with a small energy barrier may not lead to a transition state. The strong interaction of the diabatic surfaces is the result of the fact that the charge-transfer configuration H^+CN^- is common to the two configuration packets associated with the two diabatic surfaces and has a significant weight in both. In other similar problems where the surfaces do not interact so strongly, one could expect a minimum to occur separated by two transition states.

As a second example we shall consider the reactions (eq 4 and 5) corresponding to [1,2]- and [1,3]-sigmatropic shifts in propene.

$$H_2C{=}CH(CH_3) \xrightarrow{1,2} \dot{C}H_2CH_2\dot{C}H_2 \tag{4}$$

$$H_2C{=}CH(CH_3) \xrightarrow{1,3} CH_3CH{=}CH_2 \tag{5}$$

The geometry of a forbidden supra transition state has been determined by Radom et al.[14] at the SCF level: it corresponds to an almost planar allyl moiety with the migrating hydrogen situated above the central carbon atom (C_s symmetry). The geometry of the $\dot{C}H_2CH_2\dot{C}H_2$ diradical has been determined by Morokuma et al. at the MC-SCF level.[15]

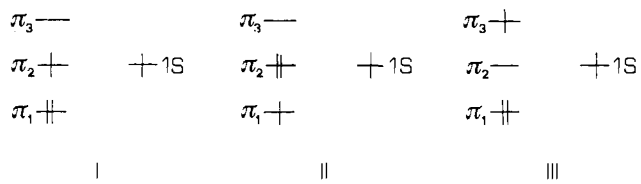

Figure 3. IFC required for the description of ground (I) and excited state (II + III) of the allyl fragment plus hydrogen.

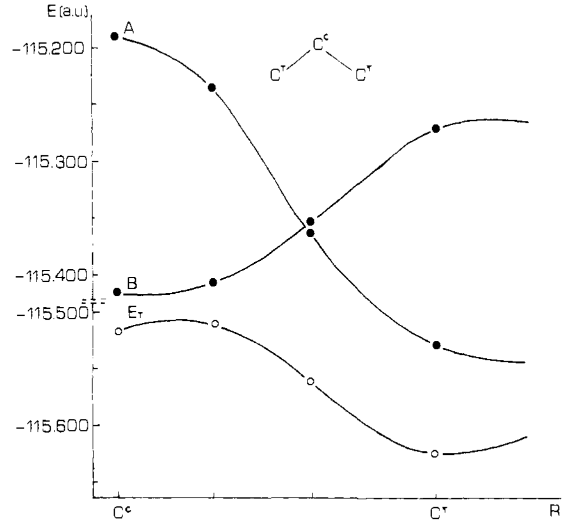

Figure 4. Diabatic (A and B) and adiabatic (E_T) curves in a plane perpendicular to the CCC plane and containing the CC bond axis. A denotes the diabatic curve associated with the IFC I and B that associated with the IFC II and III.

The fragment decomposition chosen here involves an allyl radical fragment and an hydrogen atom. The valence orbitals are the three allyl π orbitals and the 1s hydrogen orbital. Propene correlates with the ground state of the allyl fragment plus hydrogen, while $\dot{C}H_2CH_2\dot{C}H_2$ and the supra transition structure correlate with an excited state of the allyl radical plus hydrogen. The ground state of the allyl fragment plus hydrogen can be represented by configuration I (see Figure 3), while the excited state of the allyl radical plus hydrogen is represented by an almost equal admixture of configurations II and III. Thus we can represent the migration of an H atom from propene to $\dot{C}H_2CH_2\dot{C}H_2$ or to the supra transition structure in terms of two diabatic surfaces, one associated with the packet including the IFC I plus the related one-electron CTC and the other with the packet including the IFC II and III and the related one-electron CTC.

The behavior of these diabatic surfaces in the plane containing the C–C bond and perpendicular to the allyl plane is shown in Figure 4 along with the corresponding adiabatic surface computed with the full CI. These computations refer to a hydrogen atom moving along the C–C bond at a fixed distance of 1.1 Å above the bond and with the allyl framework kept at the geometry fully optimized at the STO-3G MC-SCF level.[16] One observes an intersection between the two diabatic curves and in correspondence the total energy curve has a maximum. Thus one expects to find a transition state for a [1,2] shift. Furthermore the supra structure of Radom et al. should lie on the surface of the $\dot{C}H_2CH_2\dot{C}H_2$ molecule, which shows a minimum when the hydrogen is in the region of the central carbon atom. We have subsequently performed full geometry optimizations at the MC-SCF level and

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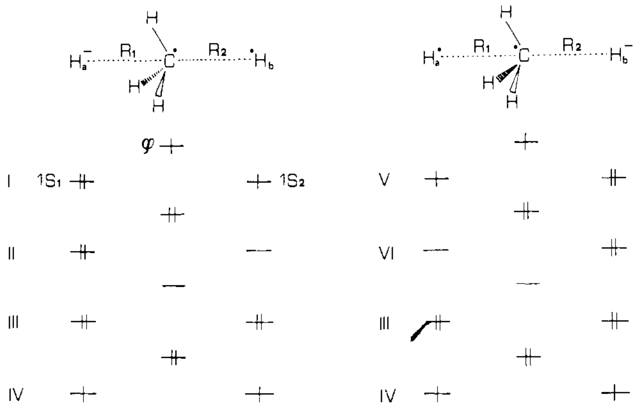

Figure 5. Bonding situations and related IFC, and CTC for a three-fragment decomposition in a S_N2 nucleophilic displacement.

found that the supra structure collapses to $\dot{C}H_2CH_2\dot{C}H_2$ and that a well-defined transition state exists for the [1,2] shift.[16]

It can be seen that the diabatic curves for hydrogen migration in HCN and in the [1,2] shift in propene exhibit many similar features. In both examples the avoided intersections correspond to intersections of diabatic surfaces that correspond to ground and excited states of one of the fragments. Also, in each case we have two intersections: for the H migration in HCN the two intersections are not symmetric and one finds only one transition state, while, in the case of the H migration in propene, they are symmetric and separated by a minimum. For HCN there is a maximum in the curve corresponding to the diabatic surface associated with the $^2\Sigma^+$ CN state and a similar maximum occurs also in the curve associated with the packet including IFC I of the allyl fragment; however, in HCN this maximum corresponds to the intersection of the two $^2\Sigma^+$ surfaces while in propene it is purely repulsive.

3.2. S_N2 Reactions. As a model S_N2 reaction for a nucleophile displacement, we consider

$$H_a^- + CH_3H_b \rightleftharpoons H_aCH_3 + H_b^- \qquad (6)$$

The choice of the fragments and the identification of the diabatic surfaces involved in this problem is not so obvious as in the previous cases. Recently Shaik[7] has analyzed the S_N2 reactions in much detail and has shown that at a qualitative level a two- and three-fragment model are equivalent. However, for a quantitative analysis of the type presented here a three-fragment model is essential, since only in this model the fragment orbitals retain their character along the reaction coordinate. Thus the three fragments are two hydrogen atoms and a CH_3 radical and the valence orbitals are the two hydrogen 1s orbitals and the singly occupied orbital of the CH_3 fragment (φ). The reactant IFC is configuration I in Figure 5, while the product IFC is configuration V. Then the "bonding situation" in the reactant is well described by the IFC I plus the CTC II, III, and IV and corresponds to a situation where the two-electron bond R_2 is gradually broken while the three-electron bond R_1 is gradually formed. On the other hand the "bonding situation" in the products, described by the IFC V plus the CTC VI, III, and IV, is the opposite: here it is the two-electron bond R_1 that is broken and the three-electron bond R_2 that is formed.

The behavior of the two related diabatic curves is shown in Figure 6, along with the total-energy curve computed with the full CI. These computations have been performed at various points of the reaction path determined by Morokuma et al.[13] It can be seen that the two diabatic curves do correlate correctly with reactants and products. The energy difference between the diabatic curve and the adiabatic energy curve at the asymptote (taken here at R_1 = 2.76 and R_2 = 1.10 Å for reactants and at the interchanged values for the products) is just 2.6 kcal/mol. The curves must intersect at the transition state by construction in this symmetric case.

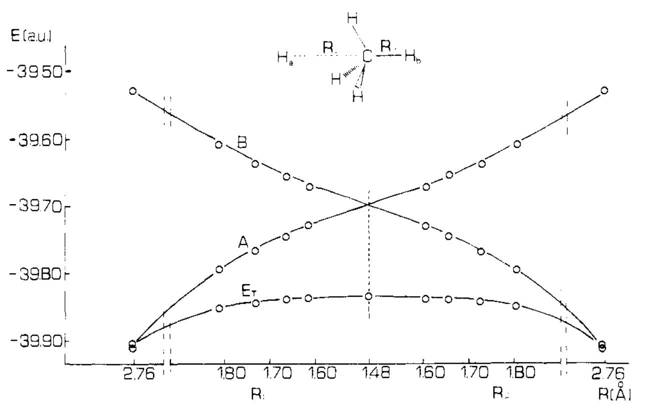

Figure 6. Diabatic (A and B) and adiabatic (E_T) curves for a three-fragment decomposition in a S_N2 nucleophilic displacement.

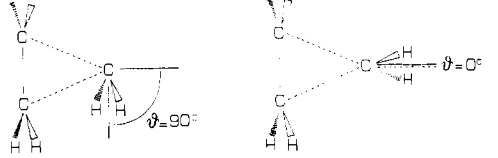

Figure 7. Unsymmetrical (ϑ = 90°) and symmetrical (ϑ = 0°) approaches of a bent methylene to an ethylene.

Table I. CI Expansion Coefficients for Diabatic (A,B) and Adiabatic (T) States for H^- + CH_4

configurations	expansion coefficients					
	R_1 = 2.76, R_2 = 1.10			R_1 = 1.73, R_2 = 1.30		
	A	B	T	A	B	T
I	0.77		0.77	0.79		0.64
II	−0.51		−0.50	−0.35		−0.25
III	−0.38	−0.03	−0.39	−0.40	0.23	−0.40
IV	0.04	0.80	0.08	0.31	0.68	0.45
V		−0.59	−0.06		−0.67	−0.40
VI		−0.02	−0.00		−0.17	−0.08

In Table I we have listed the CI expansion coefficients at two points on the reaction path: namely, at the asymptote and at a point half way to the transition state. It can be seen that at the reactants geometries the lower curve is dominated by configuration I and the upper curve by configuration IV. At the transition state the diabatic curves are dominated by configuration I and IV in one case and V and IV in the other. The energy difference from the adiabatic curve at this point (80.5 kcal/mol), due to the mixing of the two diabatic curves, can be easily interpreted. The reactant diabatic curve corresponds to a deformation where only the breaking of the bond R_2 occurs without allowing the electron pair bond R_1 to form. Thus the energy difference with the adiabatic curve represents the energy stabilization of the second bond formed.

3.3. Addition of Singlet Methylene to Ethylene. As an example of a cycloaddition reaction, we consider here the addition of a bent methylene in the $^1A_1$ state to an ethylene. This reaction has been studied with extended basis sets at the CI level by Kutzelnigg et al.,[17] who have found that there is no overall reaction barrier. They have found also that the reaction path involves two mechanistically different phases, an initial "electrophilic phase" corresponding to a 90° attack of methylene (see Figure 7) and a final "nucleophilic phase" characterized by a 0° approach of methylene and by a significant C–C stretching.

The fragments here are methylene and ethylene and the valence orbitals are the π and π^* orbitals of ethylene and the σ and p orbitals of methylene (see Figure 8). The reactant IFC (configuration I in Figure 8) involves the singlet states of the two fragments, while the product IFC (configuration II in Figure 8) corresponds to a triplet state of ethylene and a triplet state of

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(17) Zuranski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654–2659.

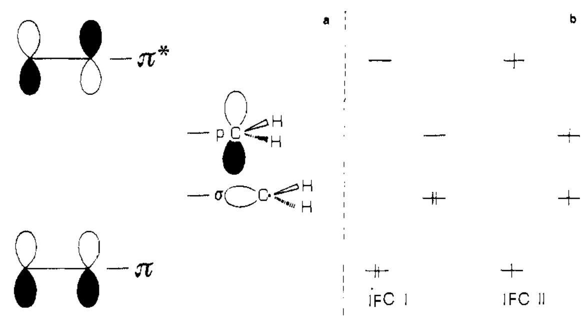

Figure 8. Valence orbitals for the addition of methylene ($^1A_1$) to ethylene (part a) and IFC associated with reactants and products (part b).

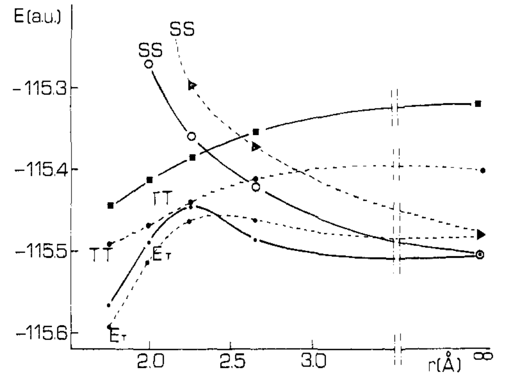

Figure 9. Diabatic (SS and TT) and adiabatic (E_T) curves for a symmetrical approach of a bent methylene to ethylene computed with an ethylene C–C bond appropriate to the ground state (full lines) and to the triplet state (dashed lines). SS denotes the diabatic curve associated with IFC I and TT that associated with IFC II.

methylene with the overall spin coupled to a singlet. Thus the two diabatic surfaces are associated with these two IFC plus the related one electron CTC. We refer to the diabatic surface associated with IFC I as the singlet–singlet (SS) surface and to that associated with IFC II as the triplet–triplet (TT) surface. The behavior of these diabatic curves for various types of methylene approach is illustrated in Figures 9 and 10 along with the corresponding adiabatic curves computed with the full CI. These computations have been performed, using the geometries of the two separated fragments optimized in ref 17. In order to obtain information about the effect of geometrical changes upon the diabatic curves, we have also performed computations where the ethylene geometry has a stretched C–C bond (r_{CC} = 1.49 Å) appropriate to the triplet excited state.

We consider first a symmetrical approach, i.e. an approach of methylene involving attak at the center of ethylene with the methylene at a 0° angle (see Figure 7). The related diabatic and adiabatic curves computed with ethylene geometries appropriate to the singlet and triplet states, are shown in Figure 9. Here, in both cases, there is an intersection of the two diabatic curves in the region of the maximum of the adiabatic curve, which causes a well-defined transition state with a significant energy barrier. With a stretched ethylenic C–C bond, the intersection occurs earlier, because the SS asymptote is raised and the TT one is lowered. As a consequence, for distances between the two fragments greater than 2.5 Å where the SS diabatic curve is dominant, the adiabatic curve with the lowest energy is that associated with the ground-state ethylene geometry, while at shorter distances where the TT diabatic curve is dominant, the adibatic curve with the lowest energy becomes that associated with the stretched ethyelnic CC bond. Here the intersection of the two adiabatic curves is not real, since they represent different cross sections of the whole surface.

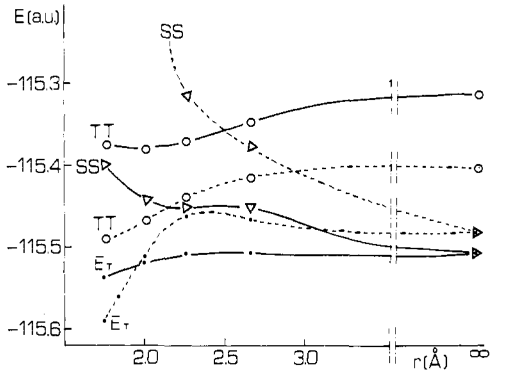

Figure 10. Diabatic (SS and TT) and adiabatic (E_T) curves for an unsymmetrical (full lines) and a symmetrical (dashed lines) approach of a bent methylene to ethylene. SS denotes the diabatic curve associated with IFC I and TT that associated with IFC II. In the symmetrical approach ethylene has a stretched C–C bond appropriate to the triplet state.

In Figure 10 we show the corresponding curves (full lines) for an unsymmetrical approach of methylene, involving again attack at the center of ethylene but with the methylene tilted by 90° (see Figure 7). It can be seen from the curves in Figure 10 that in this case there is no intersection between the two diabatic curves, and the adiabatic curve shows only a very shallow maximum.

Information about the reaction path can be obtained by comparative analyses of the curves associated with both approaches, symmetrical and unsymmetrical. To this purpose in Figure 10 we show also the curves for a symmetrical approach (dashed lines) where the ethylene geometry has a stretched C–C bond. It can be seen that for distances between the two fragments greater than 2 Å, the unsymmetrical approach is favored, while at smaller distances a symmetrical approach involving a stretched C–C bond is preferred. Again the intersection of the two curves is not real, since they correspond to two different geometries of the fragments. A similar interpretation has to be given also to the intersection between the two dominant diabatic components, i.e., the SS unsymmetrical and the TT symmetrical diabatic curves, which intersect at ~2.2 Å. This analysis also better clarifies the nature of the two mechanistically different phases of the reaction path found by Kutzelnigg et al.: in fact the reaction path involves an initial "electrophilic" phase on a surface dominated by the SS unsymmetrical diabatic surface and a final "nucleophilic" phase on a surface dominated by the TT symmetrical surface.

4. Conclusions

The main feature of the definition given in the present paper is that each diabatic surface is associated with a specific bonding situation and thus with a specific packet of configurations, i.e., with a subset of IFC and related one-electron CTC built from the valence orbitals of the fragments. A procedure is also described for the computation of these diabatic surfaces in the framework of a CI approach. Therefore the relative weight of the various configurations in a packet associated with a diabatic surface is determined by the computation and usually varies more or less at each point of the surface under investigation. This computational procedure is applied here for illustrative purposes to a variety of reactivity problems. It is shown that this type of quantitative analysis provides a clear understanding of the origin of the various critical points occurring into adiabatic surfaces. The information provided by this analysis is also very useful at a computational level for defining the region of interest where detailed geometry optimizations have to be performed for the determination of the geometries of transition states and intermediates.

Registry No. HCN, 74-90-8; $H_2C{=}CH(CH_3)$, 115-07-1; H^-, 12184-88-2; CH_3-H, 74-82-8; methylene, 2465-56-7; ethylene, 74-85-1.