

range from $r_2/r_1 = 0.5$ to 2.0 in the left-hand quadrant, they are squeezed to values of r_2/r_1 between 0.5 and 0.1 ($Z = 1$) and between 0.6 and 0.4 ($Z = 2$).

Introduction of an inner core will not change these considerations. They will cause the equipotentials to be even steeper inside the core and tend to squeeze them closer together in the left-hand quadrant.

Slater in his summary of the work on the helium atom⁸ concluded that no wave function that neglected the angular correlation of electrons could accurately represent the real wave function. Work by many authors which he summarized⁸ have shown that higher terms in the hydrogenic set of eigenfunctions were very inefficient in reproducing even the simplest function of Hylleraas which included explicitly a r_{12} term.

A final question we should like to address concerns the significance of the simple model we have constructed. The wave functions derived from this model are hydrogenic in type and contain no correlation between electrons. Why should they be any improvement over the minimized wave functions derived from

the simple variational theory? The simplest answer is that they may not. What we have done is to replace the exact potential containing the r_{12} coupling term by an approximate potential in which the r_{12} term is replaced by an angular minimum. Our solution is a solution to this approximate potential, not to the exact potential. It will be an improvement over the variational treatment only to the extent that we have guessed an improved angular minimum position. Variational treatments will average hydrogenic wave functions over the true potential and because of their neglect of correlation will always overestimate the r_{12} term. If we have guessed poorly, our solution may underestimate the r_{12} term. No general theorem exists to tell us whether or not this is the case.

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Theoretical Study of FC_2H_4

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Large-scale multireference configuration interaction (MRD-CI) calculations in a quite flexible AO basis are employed to study the energy hypersurface for the reaction intermediate FC_2H_4 . The reaction $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{FC}_2\text{H}_4$ as well as the 1,2 migration of the fluorine atom in FC_2H_4 is investigated. In addition the rotation around the CC bond in the optimum conformation is studied. The absolute minimum in the potential energy is found for the asymmetric structure but the symmetric structure is also found to be stable with respect to the dissociation, so that a shuttling of the fluorine atom is in principle possible but highly unlikely because (1) the activation energy is high (115–130 kJ/mol) and the saddle point lies only 40–50 kJ/mol below the dissociation limit of $\text{F} + \text{C}_2\text{H}_4$ and (2) the competitive motion, i.e., rotation around the CC axis, is nearly free (11–17 kJ/mol).

Introduction

The reaction of ethylene with a free radical containing one unpaired electron has been the subject of numerous experimental and theoretical investigations. In particular many ab initio calculations of different quality have been undertaken in the past to describe the reaction of ethylene with free radicals such as hydrogen, fluorine, chlorine, or OH, NH_2 , SH, and PH_2 .^{1–14} In addition theoretical studies for three-electron systems simulating

such compounds have been performed in this connection.^{15–17} In the lighter systems containing hydrogen, fluorine, OH, and NH_2 , the emphasis was primarily on the reaction path leading to the minimum in an asymmetric XC_2H_4 structure, whereas in heavier systems the 1,2 migration and bridging effect, i.e., the shuttling motion of the radical between the two carbon centers, is also of considerable interest. For the 1,2 hydrogen migration in the ethyl radical ab initio POL-CI calculations have been performed by Harding,¹⁸ for example.

From the experimental side many studies by typical chemical methods,¹⁹ electron spin resonance^{19–22} and molecular beam experiments^{23,24} have been undertaken to elucidate the situation.

In the series containing H, F, Cl, and Br the fluorine–ethylene system can be considered a branching point because anchimeric

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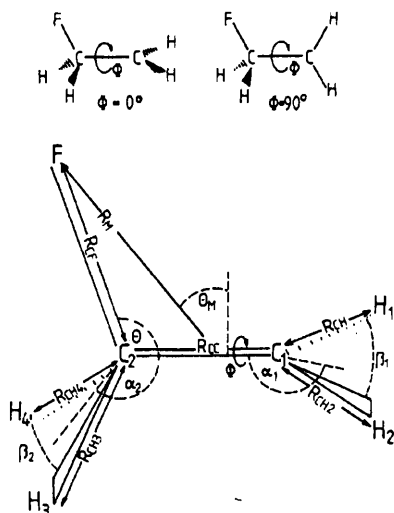


Figure 1. Definition of parameters and coordinate system employed in the present work.

and stereoselective effects are only known for systems containing heavier atoms, whereas on the other hand its electronic structure seems more similar to the chlorine and bromine compound than to $\text{H-C}_2\text{H}_4$. The theoretical investigations of the $\text{F-C}_2\text{H}_4$ system are mainly limited so far to sections of the potential surface in which the asymmetric structure, i.e., the minimal energy path, is involved.³⁻⁶ In addition, a number of dynamical studies for the reaction $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3\text{F} + \text{H}$ are found in the literature. They are generally based on quantum mechanical or modified quantum mechanical potentials as, for example, the Monte Carlo classical trajectory study of Hase and Bhalla,²⁶ or alternatively on model potentials like the R-matrix type approach by Zovijac and Light.²⁵ An investigation of the conformational preferences in substituted ethyl radicals has also been undertaken.⁷

In the present work both aspects, the reaction $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{FC}_2\text{H}_4$ as well as the 1,2 migration of the fluorine atom in FC_2H_4 , will be investigated. In addition the rotation around the CC bond in the optimum conformation will be studied. We will employ large-scale configuration interaction calculations which take into account the effect of electron correlation and are thus in principle able to furnish a reliable potential surface in the entire region of $\text{F-C}_2\text{H}_4$ nuclear conformations. The interpretation will be undertaken in terms of MO diagrams resulting from the SCF calculations preceding the CI treatments; possible interactions of the ground state with excited states which affect the ground-state surface will also be pointed out.

In subsequent papers a similar research on the compounds $\text{Cl-C}_2\text{H}_4$ and $\text{Br-C}_2\text{H}_4$ will be presented and similarities and differences between the three systems will be discussed. The results of the present work are an extensive continuation of a previous paper¹¹ which already contains some of our results but lacks all analysis of the occurring effects.

Method of Calculation

The coordinate system employed in the present work is given in Figure 1.

A first set of calculations has been carried out employing a (9s5p) set of Gaussians given by Huzinaga for the carbon atoms in the [4s2p] contraction suggested by Dunning.²⁸ For hydrogen, the five-component expansion by Whitten²⁹ was used in the [2s] contraction with a scaling factor of $\eta^2 = 2.0$. For the fluorine the standard (9s5p) basis by Huzinaga in the [4s2p] contraction suggested by Dunning²⁸ was chosen.

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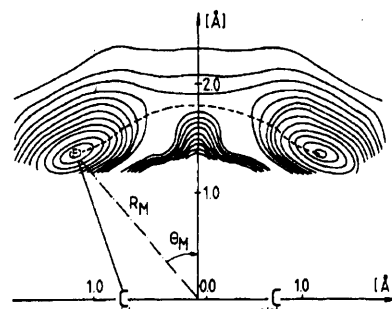


Figure 2. Calculated contour plot for the potential energy surface of FC_2H_4 in the θ_M, R_M coordinate system. The geometrical parameters are optimized for each (θ_M, R_M) pair as discussed in the text. The minimum energy path for 1,2 migration is indicated.

In order to obtain an adequate description of the CC bond, an additional s bond function with exponent $\alpha(s) = 1.4$ was located between the two carbon atoms. Similarly a bond s function with exponent 1.3 was placed in the middle between the halogen and the center of the CC bond. Various checks were undertaken to determine and account for the effect of this choice versus the arrangement in which this function is placed between the carbon center C_2 and F. After the first calculations it became obvious that d functions are also required for a proper description of polarization and correlation; hence d functions with exponents 0.7 were added to the carbon and fluorine set. The total number of contracted Gaussian in the final basis is thus 58.

In all calculations the SCF solution was first determined for the lowest state, and the corresponding orbitals were then employed as basis for the ensuing configuration interaction calculations. A core of three MO's, corresponding to the K shells of fluorine and the carbons, respectively, was always kept doubly occupied while the three MO's with highest orbital energies have been discarded entirely in the CI treatment. Hence the CI correlates 19 electrons which are distributed among 52 possible orbitals.

Generally two different type of CI calculations are undertaken, one with only a single and the other with a large number of reference configurations. The total MRD-CI configuration spaces which arise from single and double excitations with respect to the reference configurations were in the order of 800 000; the SD-CI space was around 100 000. The MRD-CI and estimated full CI (multireference analogue of the Davidson correction) energies are evaluated in the standard manner,³⁰ whereby the secular equations actually solved had values in the order of 10 000 corresponding to a configuration selection threshold of $10 \mu\text{hartrees}$.

In the region of $R_{\text{CF}} = 3.02\text{--}4.77$ au simultaneous configuration selection was also undertaken with respect to two states; i.e., additional two-root calculations were performed. In such a calculation the influence of excitations is tested with respect to the ground state and to an important excited state. This is necessary to describe the influence of the excited state under consideration properly.

Because of the size of the system, not all geometrical parameters have been fully optimized. First the values for α_1 and β_1 are set to their corresponding values of 180° and 118° , respectively, in ethylene. These parameters were optimized only at the extreme points of the hypersurface, i.e., for the absolute minimum and for the transition state of the shuttling motion. This can be justified because the energy depends very little on the change of these parameters. In addition, SCF calculations⁴ which optimized all geometrical parameters in the minimal energy path of $\text{F} + \text{C}_2\text{H}_4$ have observed that these parameters deviate only slightly (1° for β_1 and $3\text{--}5^\circ$ for α_1 in the barrier region) from their ethylene values.

The angle Φ is also kept to zero for all points on the surface and varied only at the absolute minimum to obtain the CH_2 rotational barrier or the corresponding distortion in FC_2H_4 . Furthermore, all CH bond lengths are chosen to be equal to 1.086

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TABLE I: Summary of the Most Important Data for the FC_2H_4 Potential Energy Surface^a

	SCF energy	MRD-CI energy	full CI energy	geometry, ^b au
absolute minimum	-177.4850	-177.848	-177.911	$R_{\text{CF}} = 2.72$, $\theta = 108^\circ$, $R_{\text{CC}} = 2.83$
saddle point	-124	-170	-165	$\alpha_2 = 130^\circ$, $\alpha_1 = 190^\circ$, $\beta_1 = 118^\circ$, $\beta_2 = 110^\circ$
for 1,2 migration, symmetric	-177.4040	-177.824	-177.866	$R_{\text{M}} = 3.46$, $\theta_{\text{M}} = 0^\circ$, $R_{\text{CC}} = 2.60$ au
dissociation	+88	-41	-51	$\alpha_1 = \alpha_2 = 176^\circ$, $\beta_1 = \beta_2 = 118^\circ$
$\text{F} + \text{C}_2\text{H}_4$	-177.4376	-177.813	-177.848	
	0.0	0.0	0.0	

^aTotal energies are given in hartree units, relative energies in kJ/mol. ^bOptimized at the estimated full CI level.

Å after test calculations had shown that variations in the CH bond length have a minor influence on the total energy. All the other parameters (α_2 , R_{CC} , and β_2) are varied and optimized for each value of θ_{M} , R_{M} , which are the leading coordinates in describing the shuttling motion and the dissociation process. The surface is constructed via a spline fit.

General Survey of the FC_2H_4 Potential Surface

The contour plot of the calculated potential energy surface for FC_2H_4 is shown in Figure 2. In comparison to our previous work¹¹ the surface is more extended and a reexamination of the absolute minimum has been undertaken; in addition, the parameters α_1 and β_2 (Figure 1) have also been optimized at the two minima with respect to all other parameters given earlier. The minimization has been performed at the estimated full CI level, just as has been done for all other optimization of geometrical parameters.

The optimal structure is found for the following geometry: $R_{\text{CF}} = 1.44$ Å (2.72 au), $\theta = 108^\circ$, $R_{\text{CC}} = 1.50$ Å (2.83 au), $\alpha_2 = 130^\circ$, $\alpha_1 = 190^\circ$, $\beta_1 = 118^\circ$, $\beta_2 = 110^\circ$. The angle Φ which describes the rotation around the CC bond is thereby kept at $\Phi = 0$; its influence will be discussed separately. The total SCF energy for the ground-state minimum in the electronic configuration $1a^2 \dots 9a^2 10a^2 1a'^2 \dots 3a'^2$ is -177.4850 hartrees while the MRD-CI energy is -177.878 hartrees and the estimated full CI gives -177.911 hartrees. The energy lowering by going from $\alpha_1 = 180^\circ$ to $\alpha_1 = 190^\circ$ is only about 4 kJ/mol; a decrease of α_1 below the value of 180° yields a sharp increase in total energy. From this result the FC_2H_4 radical can be characterized as a σ radical possessing a very small energy difference to the π configuration. The present values for the minimal structure are quite similar to those obtained in two earlier calculations.^{4,5} Within our error limits the geometrical parameters are the same regardless whether the estimated full CI is based on the MRD-CI or SD-CI as it should be on theoretical grounds; furthermore they do not differ from the MRD-CI values to the estimated full CI parameters.

The saddle point of the shuttling motion was also reoptimized but verified in the main our previous results.¹¹ The lowest energy for the symmetrically bridged structure in the estimated full CI surface is found for $R_{\text{CC}} = 1.38$ Å (2.60 au), $R_{\text{M}} = 1.83$ Å (3.46 au) and $\beta_1 = \beta_2 = 118^\circ$. The angles α_1 and α_2 show a small deviation from 180° , i.e., optimal values for $\alpha_1 = \alpha_2 = 176^\circ$. The determination of the best value for this angle is difficult, however, because the energy difference between $\alpha_1 = \alpha_2 = 180^\circ$ and $\alpha_1 = \alpha_2 = 170^\circ$ is only about 1 kJ/mol. The energy increases sharply for values of α greater than 180° and reaches already 10 kJ/mol for $\alpha_1 = \alpha_2 = 190^\circ$.

On the basis of these two optimized structures the calculated transition state of the shuttling motion lies 129 kJ/mol in the MRD-CI approach, and 114 kJ/mol if the estimated full CI energy is taken, above the absolute minimum. With respect to the separated fragments F and C_2H_4 this point is stable by about 45 kJ/mol. Table I summarizes the energy values for the extreme positions of the potential surface. It is seen that the configuration interaction is essential in describing the saddle point which is placed erroneously by 88 kJ/mol above the separated products in the SCF procedure. This is also the reason why most of the other calculations have not found a transition state for 1,2 migration below the energy of separated F and C_2H_4 . The present calculations thus predict that a shuttling motion is in principle possible in the FC_2H_4 system (without leading immediately to dissociation), but because of the high activation energy it seems very improbable.

In contrast to earlier theoretical studies³⁻⁵ our calculations find no barrier on the path between the minimum and the separated systems $\text{F} + \text{C}_2\text{H}_4$. Again this is a consequence of the more appropriate MRD-CI treatment employed in the present work as will be discussed in connection with the dissociation process. The calculated dissociation energy (Table I) is 165–170 kJ/mol. The CF bond energy in FC_2H_4 has not been established experimentally, but reasonable estimates for the CH bond energy and the heat of reaction for the transition $\text{F} + \text{C}_2\text{H}_4 \rightarrow \text{FC}_2\text{H}_3 + \text{H}$ lead to an estimate in the region of 190–200 kJ/mol.^{23,24} Such error is plausible in light of our experience with AO basis sets of the size employed in this work;³¹⁻³³ the error can be reduced by expanding this basis further. The results are consistent with estimates given in other work. Schlegel et al.^{4,5} show, for example, that the value for the dissociation energy of the CF bond changes by 43 kJ/mol in going from a 3-21G to a 6-31G* basis set. (The latter has approximately the same quality as our basis employed but lacks bond functions.) By taking account of correlation effects via second-order Møller–Plesset perturbation theory (MP2) they find that the value increases further by 73 kJ/mol to yield 195 kJ/mol. Inclusion of higher order effects should decrease this value.^{4,34,35} Hence our data actually calculated are in the range of their estimates. With respect to the error in geometrical variables it is known³¹⁻³⁵ that a basis set of double- ζ plus polarization function quality suffices to obtain reliable equilibrium bond lengths (for single bonds) and bond angles in a calculation which includes correlation effects in a method better than MP2. To obtain reliable results for double bonds the method must be improved further.³⁵ On these grounds we can expect that our calculations, employing basis sets of double- ζ quality plus polarization functions and the MRD-CI method, yield geometrical data within 0.02 Å (0.04 au) and 5° or better.³¹

The $\text{F} + \text{C}_2\text{H}_4$ Dissociation Path

The decrease in C–F separation toward the optimal FC_2H_4 structure shows several effects on the other geometrical parameters: first, a change in the angle α_2 from 180° in the separated systems to approximately 130° in the compound; second, a distinct elongation of the CC bond from the double-bond value to almost that of a single bond, and finally a change in angle β_2 from 118° to 110° , whereby this latter variation produces very little change in energy according to detailed calculations for the related ClC_2H_4 system. All three effects are expected in accordance with the trend from the sp^2 to sp^3 hybridization upon the asymmetric approach of the halogen atom. There are two possibilities for a dissociation path as can be seen from Figure 2. The first involves a path from the minimum to the area of $\theta_{\text{M}} = 0^\circ$ followed by dissociation along the symmetric path, while the second corresponds to direct $\text{F}-\text{C}_2\text{H}_4$ separation from the absolute minimum. An analysis of both separation pathways is most convenient in terms of the molecular orbitals involved. Hence the discussion will be divided into the slice of the potential hypersurface characterized by $\theta_{\text{M}} = 0$ (see

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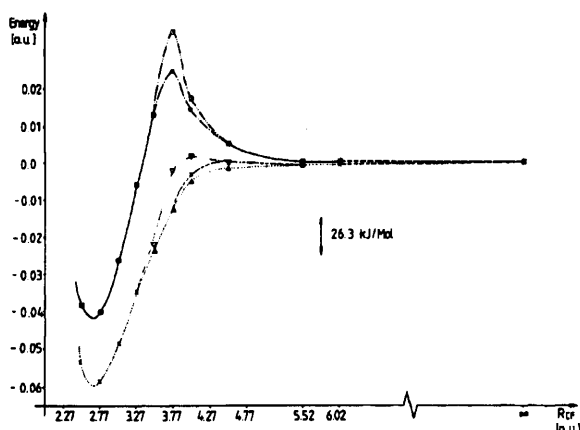


Figure 3. Calculated potential energy curve for the $\text{F-C}_2\text{H}_4$ approach along $\theta = 105^\circ$ obtained in various treatments: \odot , SCF energy, parameters optimized at the SCF level; \square , SCF energy, parameters optimized at estimated full CI level; ∇ , estimated full CI, parameters optimized at SCF level; \times , estimated full CI, parameters optimized at estimated full CI level; Δ , estimated full CI in two-root calculation, parameters optimized at estimated full CI level. The optimization is carried out for R_{CC} , α_2 , and θ_2 ($\alpha_1 = 180^\circ$, $\beta_1 = 118^\circ$, $\theta = 105^\circ$).

Figure 1) containing the transition state of the shuttling motion and into the slice with $\theta = 105^\circ$ (for the different parameters see also ref 11). This section with $\theta = 105^\circ$ through the surface is chosen because the absolute minimum of 108° is very close and differences between the $\theta = 105^\circ$ and $\theta = 108^\circ$ section can be neglected. The change from $\theta = 105^\circ$ in the MO diagram to $\theta_{\text{M}} = 0^\circ$ will be essential for the MO analysis of 1,2 migration.

1. *The Potential Surface Section $\theta = 105^\circ$.* The direct separation into F and C_2H_4 from the absolute minimum is best described by parameters R_{CF} and θ rather than by R_{M} and θ_{M} ; the conversion between the various parameters is contained in Table IIa.

The energy path for $\theta = 105^\circ$ was calculated by five different treatments. Figure 3 shows the results. In principle, two different geometrical pathways, optimized at the SCF and the estimated full CI level respectively, are combined with three different calculation procedures. In all treatments the energy path exhibits a deep minimum with R_{CF} variation. The values for the geometrical parameters at this minimum are the same as those given above for the absolute minimum (with the exception of θ chosen to be 105° instead of 108°).

The most remarkable difference between the CI and SCF curves is the very high energy barrier of about 65 kJ/mol predicted by the SCF treatment (in the SCF geometry) which is removed by the more appropriate CI method. This behavior points to a crossing of two or more single-configuration states in this region, as has been discussed for the analogous approach of $\text{NH}_2 + \text{C}_2\text{H}_4$,¹ so that a quantitative description of the energy surface requires a multiconfigurational (MRD-CI) wave function. The SCF barrier is enhanced if the geometries optimized at the estimated full CI level are employed, which is understandable since this geometry is less approximate for the SCF treatment. The configuration interaction procedure removes the barrier to a large extent if the SCF geometry is used; the barrier disappears entirely if the geometries are optimized at the estimated full CI level. The most appropriate treatment in such a situation of an avoided crossing of two states is a two-root MRD-CI treatment, which has also been undertaken in the barrier region. Such procedure considers both states involved equally well and possesses therefore a more balanced space in the truncated CI matrix than occurs if one of the states is preferentially treated; this in turn allows also for a more reliable estimate of the full CI energy. In areas further away from the avoided crossing the results of a two-root and one-root MRD-CI calculation are identical for the lowest state. The optimal geometries for the FC_2H_4 structures along the SCF barrier region are given in Table IIb. It is obvious that between $R_{\text{CF}} = 3.77$ and 4.52 au the optimal geometrical parameters are

TABLE II: (a) Conversion between the Parameters R_{CF} , θ and R_{M} , θ_{M} Using the Optimal R_{CC} Value. (b) Comparison of the Optimized Geometries from the SCF Calculations with the Optimized Geometries from the Estimated Full CI Calculations

a				
θ , deg	R_{CF} , au	$R_{\text{CC}}^{\text{opt}}$, au	R_{M} , au	θ_{M} , deg
105	2.52	2.88	2.74	27.3
105	2.77	2.83	2.94	24.5
105	3.02	2.79	3.16	22.6
105	3.27	2.73	3.32	17.9
105	3.52	2.70	3.60	19.2
105	3.77	2.71	3.84	18.5
105	4.02	2.58	4.06	17.0
105	4.52	2.56	4.54	15.9
105	5.52	2.53	5.50	14.2
105	7.02	2.53	6.97	13.4
105	8.52	2.53	8.45	13.1

b				
R_{CF} , au	SCF geometry		CI geometry ^a	
	R_{CC} , au	α_2 , deg	R_{CC} , au	α_2 , deg
3.52	2.75	155	2.70	152
3.77	2.60	171	2.71	156
4.02	2.53	175	2.58	167
4.52	2.53	180	2.56	180
	2.53	180	2.53	180

^a Estimated full CI, two-root MRD-CI treatment.

quite different in the SCF and the CI treatment. Hence a geometry optimization at the SCF level followed by a CI calculation for these geometries would lead to different results in the area of avoided crossing. Such procedure is employed quite often and this example demonstrates quite nicely its pitfalls.

The MO correlation diagram for $\theta = 105^\circ$ is contained in Figure 4. Figure 4a gives the orbital energy diagram and Figure 4b contains the shape of the MO's for the $\text{F-C}_2\text{H}_4$ approach along $\theta = 105^\circ$; the unimportant lower lying MO's are not given. Because the molecule possesses only C_s symmetry the p_x and p_y in-plane p_x orbitals are able to mix, as seen already for the separated fluorine atom (Figure 4b). The MO's affected most in the reaction involve primarily those made up from atomic p functions, i.e., the fluorine p_x , p_y , p_z AO's and the ethylene $3\sigma_g$ -type ($3a_g$) and π (in-plane π , out-of-plane $1b_{2u}$) and π^* -type (in-plane π^* , out-of-plane $1b_{1g}$) MO's. The change in the more stable MO's ($6a'$ and lower) is conventional. Note that the orbital energy of the open-shell orbital ($10a'$) (Figure 4a) is obtained in a different field in the SCF procedure so that its energy cannot be directly compared with those of the doubly occupied species (hence the fluorine p_x is formally not degenerate with the p_y and p_z AO's). For a description of the interaction during the fluorine approach toward the ethylene, the orbitals can be separated into two groups by symmetry, whereby an interaction between the two groups of different symmetry is not possible. The first group (Figure 4b, lower part) belongs to A'' symmetry and consists of the $1b_{2u}$ and $1b_{1g}$ MO's of ethylene and the p_y AO of fluorine. All three mix in the FC_2H_4 compound and can be characterized as a CF bonding linear combination of $1b_{2u}$ and p_y ($1a''$), a nonbonding orbital ($2a''$) with a node at C_β and a CF antibonding MO ($3a''$). The orbitals of the other group belong to A' symmetry (Figure 4b, upper part). They involve the σ ($3a_g$) and π bond of ethylene and the in-plane p functions on fluorine. A rough characterization of the four MO's $7a'$ to $10a'$ in the compound is (1) the ethylene σ MO and ($p_x + p_z$) of fluorine make a CF bonding combination ($7a'$) and the equivalent CF antibonding combination ($9a'$) maintaining in each case as far as possible the CC bonding character; the bonding combination is stabilized with respect to the original $3a_g$, the antibonding combination corresponding destabilized. The π and π^* MO's of ethylene combine with the ($p_x - p_z$) fluorine combination to give the doubly occupied $8a'$ which describes the σ bond between C and F and tries to establish at the same time good CC

TABLE III: Orbital Energies of the Three Inner Shells Given for the Extrema of the Potential Energy Hypersurface (Energies in au)^a

orbital	$\theta = 105^\circ$			$\theta_M = 0^\circ$			$\Delta\epsilon_3$ of both minima
	ϵ_i (min)	ϵ_i ($R_{CF} = 40.0$ au)	$\Delta\epsilon_1$	ϵ_i (min)	ϵ_i ($R_{CF} = 40.0$ au)	$\Delta\epsilon_2$	
1s (fluor)	-26.2455	-26.3826	-0.1371	-26.2710	-26.3825	-0.1115	0.0255
σ_g (ethylene)	-11.3244 ^b	-11.2379	+0.0865	-11.2734	-11.2450	+0.0284	-0.0510
σ_u (ethylene)	-11.2465 ^b	-11.2363	+0.0102	-11.2721	-11.2437	+0.0284	-0.0256

^a $\Delta\epsilon_{1/2} = \epsilon_i(40.0 \text{ au}) - \epsilon_i(\text{minima})$. $\Delta\epsilon_3 = \epsilon_i(\text{minima } \theta_M = 0^\circ) - \epsilon_i(\text{minima } \theta = 105^\circ)$. ^b In the absolute minima σ_g becomes the 1s orbital of the C_2 atom and σ_u the 1s orbital of the C_1 atom.

bonding which places its orbital energy only slightly above that of the $7a'$. From the second linear combination the singly occupied $10a'$ orbital of FC_2H_4 results which is mostly a p orbital on the C_1 atom but shows also some spin density at the fluorine atom. The third possible combination between π , π^* , and $p\sigma_2$ leads to a higher lying unoccupied MO with CF antibonding character. The combination with the π^* is necessary in this case for describing the proper nodes in the occupied MO's. This interaction of MO's results in a charge transfer during the reaction from ethylene to fluorine. This information can also be derived from the inner-shell orbital energies 1s on fluorine and $1\sigma_g$ and $1\sigma_u$ of ethylene. By use of Koopmans' theorem³⁶ the 1s energies can be compared with the measured peaks of XPS (ESCA) spectroscopy.^{37,38} It can be shown that the higher the inner-shell orbital energy the more negative is the surrounding of the atom under consideration. Table III contains the pertinent orbital energies at important points of the potential surface. The fluorine 1s energy shows a large change from -26.3826 to -26.2455 hartrees in the combined system; hence a partial ionic structure $F^-C_2H_4^+$ is expected at the absolute minimum while the lowest dissociation channel refers clearly to entirely neutral species. The lowest state possessing the ionic structure $F^-C_2H_4^+$ is represented by the excited-state $2^2A'$ which originates in the separated species from a single excitation out of the π orbital ($9a'$) into the $10a'$ p orbital of fluorine. Hence along the reaction path interaction between these two states (and others involving the π^* MO) occur. Because of the low symmetry such mixing (avoided crossing) can already occur at the MO level rather than at the configuration level. Note, however, that the charge transfer is not complete at the minimum.

Even though the low symmetry makes the state mixing possible, the single-configuration SCF wave function is not able to fully describe the interaction as seen in Figure 3; the SCF potential curve shows a barrier in the interacting zone while the CI procedure removes this hump entirely. The present form of the potentials obtained in the CI treatment is in contrast to earlier studies.³⁻⁵ Clark et al.³ employing the RHF and UHF SCF formalism with a 4-31G AO basis find a barrier height (relative to the separated species) of 13 kJ/mol using the UHF and 46 kJ/mol in the RHF SCF method at an F-C distance of 2.1 Å (3.97 au). Schlegel⁴ predicts a barrier at CF = 1.93 Å (3.65 au), the height of which depends on the treatment. These calculations are in accord with the results of the present RHF SCF calculations exhibiting erroneously a barrier at 2.0 Å (3.80 au) with 65 kJ/mol. On the other hand, the indication that the previously reported barriers are an artifact of the theoretical treatments can be obtained by an analysis of the various computational procedures. The calculated barrier for fluorine addition to ethylene decreases if the formalism is improved. RHF SCF calculations obtain barriers, while the UHF treatment, which allows for some configuration mixing on the orbital level in the low C_2 symmetry, leads to a smaller barrier of only 13-15 kJ/mol.^{3,5} Addition of Møller-Plesset (MP) perturbation theory on the UHF treatment reduces the barrier further. It is known, however, that in the region of the transition complex the Møller-Plesset perturbation series exhibits only slow convergence.^{39,40} MP2 to MP4 calculations

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	$\theta = 105^\circ$	$\theta_M = 0^\circ$
character a''	1a'' F-C-C bonding	1a ₂ nonbonding
	2a'' nonbonding	1b ₁ three-center bonding
	3a'' FC antibonding	1b ₁ three-center antibonding
	CC antibonding	CC bonding
character a'	7a' three-center-type bond	5a ₁ nonbonding
	9a' CF (π -type) antibonding	4b ₂ nonbonding
	CC bonding	
	8a' CF (σ -type) bonding	6a ₁ three-center bonding
	CC bonding	
	10a' nonbonding	7a ₁ three-center antibonding
	singly occupied	singly occupied

predict, for example, a barrier in the reaction of OH to C_2H_4 which is not present any more in calculations using the projected spin formalism.⁴¹ The H + C_2H_4 barrier is also overestimated if the MP4 procedure is employed.⁴² On the other hand, MRD-CI formalism is adequate for the description of interacting states^{31,32} and hence we believe that there is no barrier in the F + C_2H_4 minimal energy path.

2. *The Symmetric Approach at $\theta_M = 0^\circ$.* The potential curve in the SCF approach of F + C_2H_4 at $\theta_M = 0^\circ$ is repulsive (Figure 5). CI calculations show a flat minimum of 48 kJ/mol at $R_M = 1.83$ Å (3.46 au), i.e., at a CF distance of 1.95 Å (3.68 au). The optimal geometrical parameters for this minimum are $R_{CC} = 1.38$ Å (2.60 au) and $\alpha_1 = \alpha_2 = 176^\circ$. The calculated MRD-CI energy is -177.828 hartrees, the estimated full CI -177.866 hartrees.

The orbital energies for the separated and the combined molecule as well as the main features of the MO's involved are contained in Figure 6. While Figure 6a gives the orbital energy diagram, Figure 6b contains the shape of the involved MO's for the symmetric approach along $\theta_M = 0^\circ$. Because of the higher C_{2v} symmetry the orbital groups which can interact with one another must be divided further. The three a'' MO's known from the $\theta = 105^\circ$ section separate into b_1 and a_2 symmetry. The in-plane π^* -type ethylene orbital classified as $1a_2$ remains unchanged during the F- C_2H_4 approach while the $1b_{2u}$ mixes with the fluorine p_y AO to give a positive and negative linear combination $1b_1$ and $2b_1$ of Figure 6b.

In the second group of orbitals the p_x fluorine AO transforms according to the B_2 irreducible representation while p_z is of A_1 symmetry. Because of these symmetry rules and energetic reasons mixing occurs only between the ethylene π ($6a_1$) and fluorine p_z ($7a_1$) MO to give the positive and negative linear combinations as seen in the figure. Thus for $\theta_M = 0^\circ$ the nonbonding open-shell orbital $10a'$ (Figure 4) of $\theta = 105^\circ$ is replaced by the F- C_2H_4 antibonding combination $7a_1$ and the π bond between fluorine and carbon C_2 ($8a_1$) is replaced by a three-center bond ($6a_1$). Out of symmetry reason the π^* orbital is not involved in the bonding mechanism. A comparison of the various effects in the higher and lower molecular symmetry is contained in Table IV and the weaker binding between F and C_2H_4 for $\theta_M = 0$ is also expected on this qualitative basis.

Because the fluorine approaches both carbons in this symmetry the nuclear repulsion increases faster with decreasing separation

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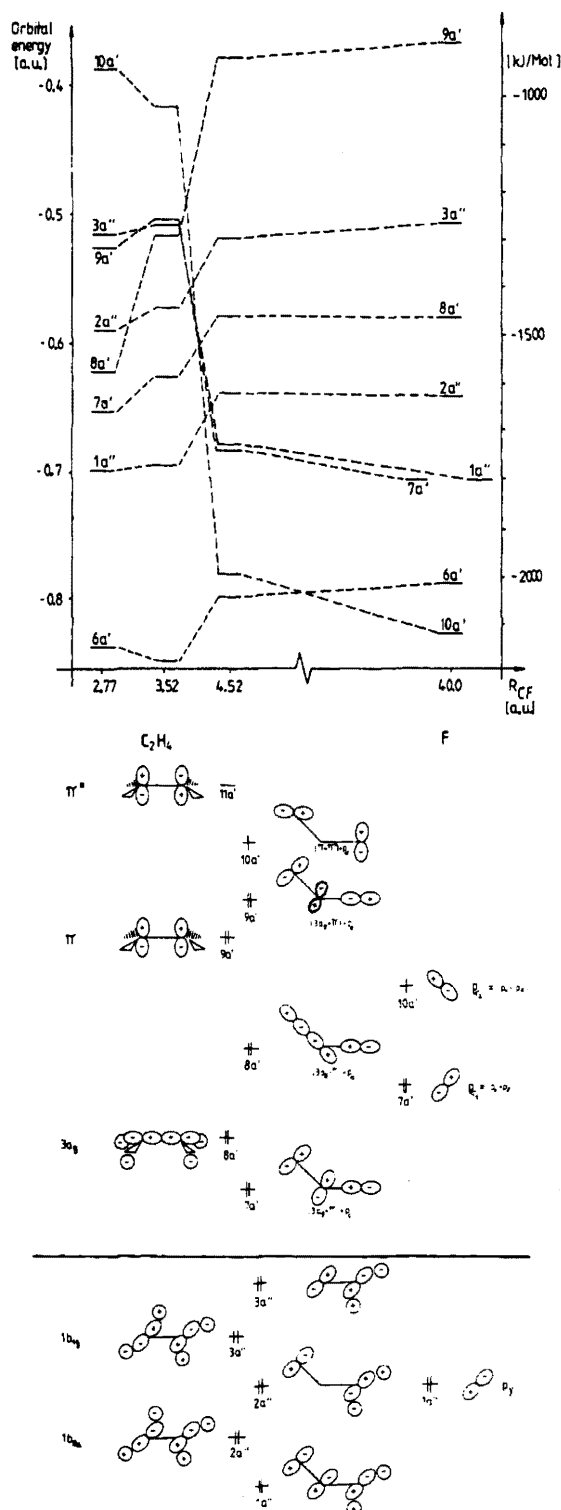


Figure 4. (a) Orbital energy diagram for the $\text{F}-\text{C}_2\text{H}_4$ approach along $\theta = 105^\circ$. (b) Orbital correlation diagram for the $\text{F}-\text{C}_2\text{H}_4$ approach along $\theta = 105^\circ$.

than for $\theta = 105^\circ$ (Table V). As a result the fluorine approaches the C_2H_4 not as closely as in the sidewise attack; on the basis of this larger separation alone, the interaction between fluorine and ethylene must be smaller than along the preferred route. This is also seen from the charge transfer between F and C_2H_4 which has taken place only to a smaller extent as can be seen from Table III in which the 1s fluorine orbital energy has changed less from

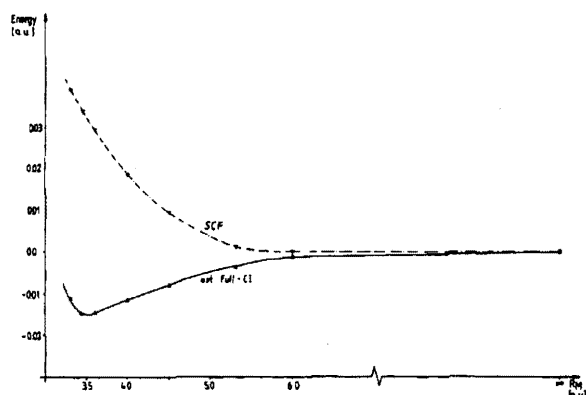


Figure 5. Calculated SCF and CI potential curves for the $\text{F}-\text{C}_2\text{H}_4$ approach along the symmetric (orthogonal) $\theta_M = 0^\circ$ approach. All other geometrical parameters are optimized at each point.

TABLE V: (a) The Behavior of the Nuclear Repulsion V_{NN} during the Symmetric Fluorine Approach. (b) The Behavior of the Nuclear Repulsion V_{NN} (in au) during the Asymmetric Fluorine Approach

a			
R_M/R_{CF}	θ_M , deg	E_{SCF} , hartrees	V_{NN} , au
3.6/4.4	0	-177.4082	68.655
3.0/3.9	0	-177.3787	73.553
2.7/3.7	0	-177.3409	77.733

b			
R_{CF}	θ , deg	E_{SCF} , hartrees	V_{NN} , au
2.52	105	-177.4758	73.237
2.77	105	-177.4778	71.338
3.02	105	-177.4637	68.850
3.27	105	-177.4437	67.549
	105	-177.4376	36.839

the separated system to the $\theta_M = 0$ minimum than to the $\theta = 105^\circ$ absolute minimum. There is no interaction between the X^2A_1 ground state and the first excited state since they are of different (B_2) symmetry.

A comparison with the $\theta = 105^\circ$ potential curve in Figure 3 suggests an explanation for the absence of an SCF minimum in the $\theta_M = 0$ curve. The potential barrier in Figure 3 is the consequence of a charge transfer or, put in different words, results from an avoided crossing of two states of the same ($^2A'$) symmetry with vastly different charge distributions. Such interaction (between X^2A_1 and 2^2A_1 states) must also be present in the C_{2v} symmetry, but if this would occur at approximately the same separation between F and C_2H_4 as is found for the asymmetric approach, the crossing would just fall into the region in which the CI calculations find a minimum in the C_{2v} approach. In other words the principal behavior of the SCF curve for $\theta = 105^\circ$ is hidden underneath the curve for $\theta_M = 0^\circ$, since the nuclear-nuclear repulsion is the dominant shape-determining factor. This interpretation is supported by the shape of the repulsive SCF curve for $\theta_M = 0^\circ$ which rises relatively slowly with decreasing $\text{F}-\text{C}_2\text{H}_4$ separation compared to that in Figure 3. From a technical point of view the description of the CI minimum requires for $\theta_M = 0^\circ$ a number of configurations in the reference set and not only one dominant species, which is again an indication for a change in character, i.e., charge transfer in this case in the neighborhood of the minimum.

Theoretical considerations for a three-electron model system¹⁵⁻¹⁷ predict a high barrier for $\theta_M = 0$ perpendicular approach. In this model the electrons are distributed into three equivalent orbitals each of them belonging to one of the centers. After elimination of the quartet state with three parallel spins two doublet states remain. The first can be interpreted in the VB sense as the resonance structure with the bond localized between centers 1-2,

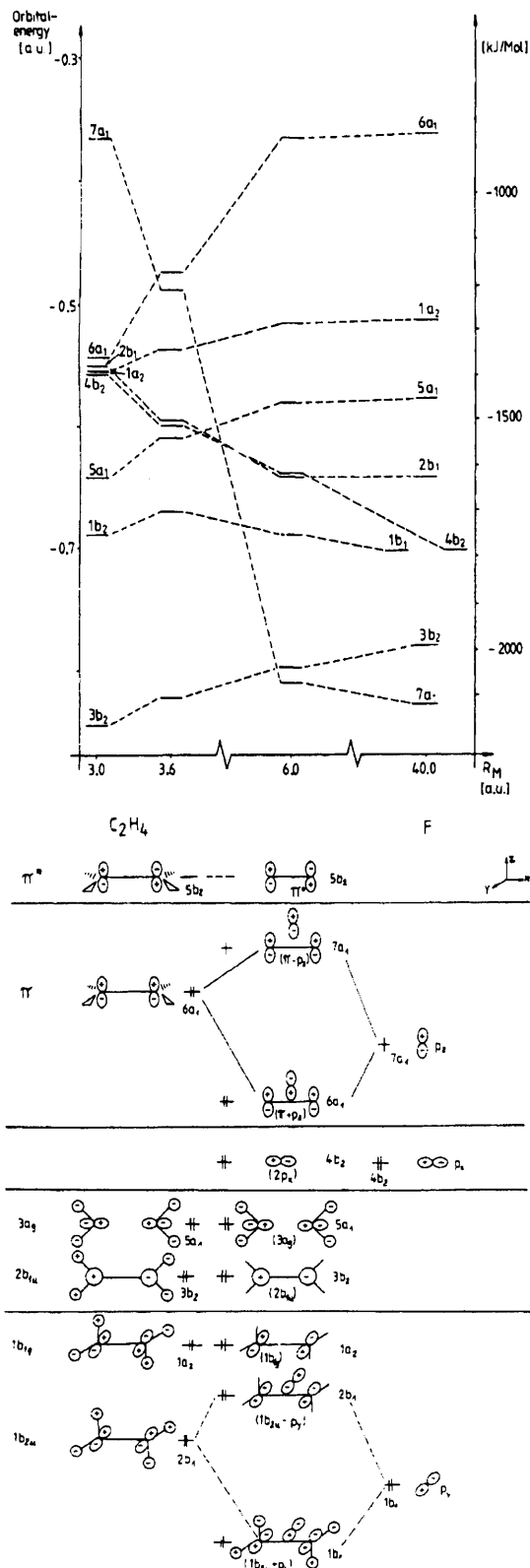


Figure 6. (a) Orbital energy diagram for the F-C₂H₄ symmetric approach along $\theta_M = 0^\circ$. (b) Orbital correlation diagram for the F-C₂H₄ symmetric approach along $\theta_M = 0^\circ$.

while the other doublet describes the linear combination of structures with 1-3 and 2-3 bonds.¹⁷ From the secular determinant for the doublet functions a surface crossing results for the equilateral triangle with the conclusion that a high barrier on the

lower surface makes this path of reaction highly improbable. The reaction described in this model corresponds to a process in which the 1-2 bond is broken during the reaction and replaced by a structure which is described by a linear combination between 1-3 and 2-3. The barrier is found in this model for a purely covalent bonding; ionic admixtures are predicted to reduce its height.

The present description of the process is entirely different. The interaction is described in terms of only two orbitals, the π of ethylene and the p_z of fluorine. Along the reaction path the two electrons of the π remain coupled which is not the case for the second doublet state in the other model. Going along the path only two MO's, the positive and negative linear combination as shown in Figure 6, are possible. The first doublet state consists then of $6a_1$, $7a_1$, i.e., double occupation of the stabilized bonding MO and single occupation of the antibonding MO, and is expected to be stabilized with respect to the separated systems. The second doublet possesses the inverse population and becomes higher in energy during reaction. Because there is no crossing between the two states our model predicts an allowed perpendicular approach without barrier. The connection to the model of Yamaguchi and Bonacic-Koutecky et al.¹⁵⁻¹⁷ could be made by considering also the π^* ethylene orbital; since this belongs to B₂ symmetry in this C_{2v} approach, mixing with the others discussed above is not possible, however. The present model thus assumes that the bond of the incoming center to the two others is weaker than the bond between those. This seems to be the more appropriate picture for the halogen-ethylene approach than that given earlier.¹⁵⁻¹⁷ It predicts bonding for $\theta_M = 0^\circ$ (under the assumption of purely covalent structure) which is only seen in the estimated full CI curve. Hoz et al.^{9,10} have discussed a similar mechanism; their MO analysis does not contain the asymmetric minimum, however. As it has been discussed above, the SCF barrier found in the present work at $\theta = 105^\circ$ results from charge transfer, which is also responsible for the small minimum in the $\theta_M = 0^\circ$ CI curve and the steady but slow raise of the corresponding SCF curve.

Rotation around the CC Bond

An additional motion to the fluorine 1,2 migration is the CH₂ rotation around the CC bond. The 1,2 migration is hindered for $\Phi = 90^\circ$ since the hydrogen of the C₁ atom would, for example, prevent the approach of the fluorine atom. A fast rotation around the CC axis would thus probably reduce the A factor in the shutting reaction.

The variation in parameter Φ was undertaken at the geometry of the minimum, with the exception that α_1 was 180° instead of its minimal value of 190° . Effects of this difference will be discussed at a later stage. Figure 7 shows that Φ variation results in an energy lowering of approximately 8 kJ/mol in the MRD-CI surface ($\Phi \approx 40^\circ$) while the effect on the estimated full CI surface is only 2-3 kJ/mol. The change in total energy is quite small in the entire region between $\Phi = 0^\circ$ and $\Phi = 90^\circ$ and it is therefore difficult to determine unambiguously the optimum value of Φ on this flat surface.

The MO correlation diagram between the two extreme positions $\Phi = 0^\circ$ and $\Phi = 90^\circ$ is contained in Figure 8. There is no major reorientation of MO's during rotation; in the main one finds localization at one or the other carbon which have different structural surroundings. Both trends, stabilization (11a, 12a) and destabilization (10a, 13a), are observed so that no qualitative conclusions can be made. The electronic part of the total SCF energy increases from -248.468 ($\Phi = 0^\circ$) to -248.365 hartrees ($\Phi = 90^\circ$) while the nuclear repulsion decreases from 70.987 to 70.88 hartrees so that the total SCF energy remains essentially unchanged. Correlation effects seem small but determine the final shape of the rotational potential curve.

The ionic character of FC₂H₄ decreases when rotation takes place. This is seen from Table VI, which summarized the orbital energies of the inner-shell orbitals at the extreme positions $\Phi = 0^\circ$ and $\Phi = 90^\circ$. The effect can be explained by the form of the open shell. For $\Phi = 90^\circ$ the odd electron is localized at C₁ while at $\Phi = 0^\circ$ there is also a small electron density at the fluorine atom (Figure 8b).

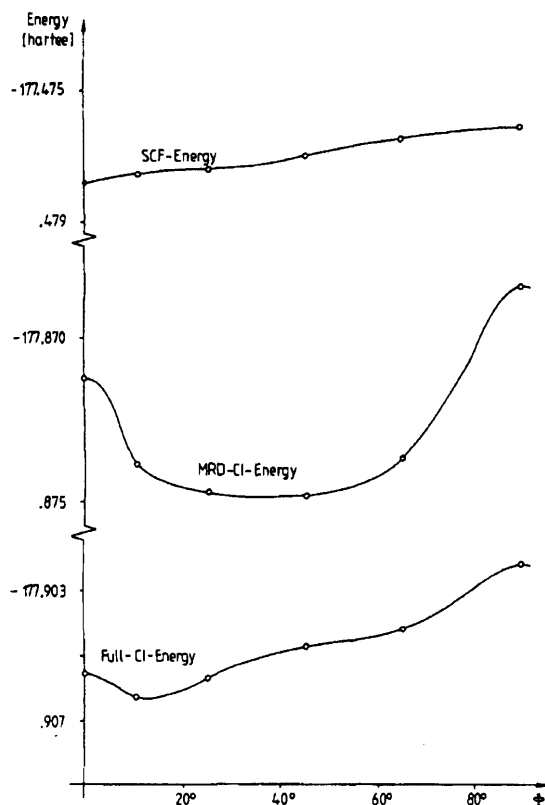


Figure 7. Calculated total energy for the optimal FC_2H_4 structure as a function of the rotational angle Φ .

TABLE VI: Inner-Shell Orbital Energies for the Extreme Points of the CH_2 Rotation (in hartree units)

	$\Phi = 90^\circ$	$\Phi = 0^\circ$	
1s fluorine	-26.2508	-26.2455	1s fluorine
1s C_2	-11.3270	-11.3244	1s C_2
1s C_1	-11.2400	-11.2465	1s C_1

All calculations of the Φ variations were performed with $\alpha_1 = 180^\circ$, even though the reoptimization of all parameters for the minimum favored a slightly pyramidal radical center ($\alpha_1 = 190^\circ$) over the planar structure. This means that the conformers change slightly from conformation I with $\Phi = 0^\circ$ to conformation Ia (Figure 9) and from structure II with $\Phi = 90^\circ$ to IIa. It is seen that the repulsion between the nuclei is reduced in going from structure II to IIa. Since the effect on the orbitals between II and IIa can be neglected one expects that the energy corresponding to a rotation with $\alpha_1 = 190^\circ$ is lowered somewhat, but the effect should be less than 2 kJ/mol based on a comparison with the 3-21G SCF calculations of Schlegel^{4,5} and Bernardi.⁷

Hence the qualitative form of the potential curve for the rotation Ia to IIa should differ very little from that discussed for rotation I to II; i.e., it is expected that a weak minimum lies between $\Phi = 0^\circ$ and $\Phi = 90^\circ$ whereby rotation is quite easy. Schlegel et al.^{4,5} have found that structure IIa is more stable than Ia by 2.5 kJ/mol using a 3-21G basis in the MP2 approach. This stabilization is only 0.8 kJ/mol with the larger 6-31G* basis in a calculation at the SCF level. A calculation of Bernardi et al.⁷ employing the 3-21G basis in the UHF procedure places II 1 kJ/mol lower than I. Since the influence of polarization functions is probably larger in the description of the rotation than electron correlation,³¹ the value obtained by using the 6-31G* basis is probably more realistic than the MP2 result in the smaller basis. The present calculations employing an AO basis of double- ζ plus polarization quality find that correlation effect slightly stabilizes conformer I over II; we assume that the same holds for Ia relative to IIa. It is conceivable, however, that at low temperatures the

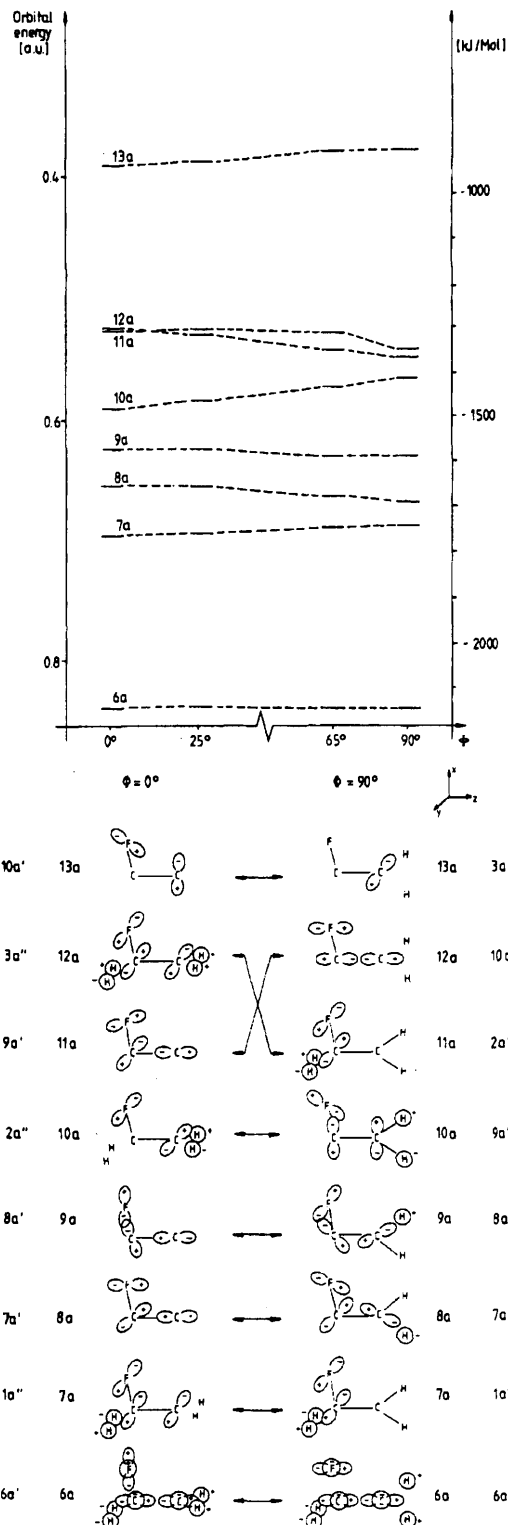


Figure 8. (a) Orbital energy diagram for the rotation around the CC bond. (b) Orbital correlation diagram for the rotation around the CC bond.

torsional motion can be confined to an average angle around $\Phi = 0^\circ$. This would agree quite well with the model given by Edge and Kochi^{20,43} on the basis of their ESR measurements.

(43) Kawamura, T.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1972, 94, 1752.

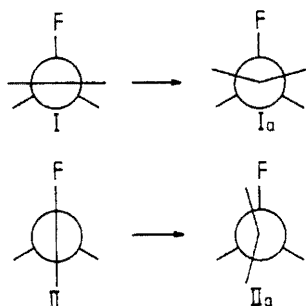


Figure 9. Schematic picture of the optimal geometrical structures involving the rotational angle Φ with $\alpha_1 = 180^\circ$ fixed (I, II) and $\alpha_1 = 190^\circ$ optimized (Ia, IIa).

Summary

The energy hypersurface for the system $F + C_2H_4$ has been calculated with special emphasis on the dissociation pathway and the 1,2 migration of fluorine. The optimization of the various geometrical parameters has been performed on the configuration interaction level; the AO basis is of double- ζ plus polarization quality.

The absolute minimum has been found for the *asymmetric* β -fluoroethyl radical. For the *symmetric* approach of F to C_2H_4 a minimum is also calculated which represents the saddle point of fluorine 1,2 migration; it lies 114–130 kJ/mol (depending on the method of calculation) above the energy of the most stable structure and is 40–50 kJ/mol below the $F + C_2H_4$ dissociation.

The calculations at the CI level find no barrier toward $F + C_2H_4$ dissociation, neither from the absolute minimum nor from the saddle point. During the approach of the fluorine a charge transfer from ethylene to fluorine occurs, the description of which requires a multiconfigurational treatment. This explains also why most

of the earlier calculations based primarily on a single-configurational procedure have predicted a barrier in the dissociation pathway and have failed to find the minimum in the symmetric $F + C_2H_4$ approach. An analysis based on MO correlation diagrams explains the qualitative features of the asymmetric and symmetric pathways.

If rotation around the CC axis is considered by varying the angle Φ , whereby all other geometrical variables are held fixed at their values corresponding to the asymmetric optimal structure, it is found that a partially rotated structure is slightly preferred over $\Phi = 0$. Since this potential curve as a function of Φ is extremely flat, however, it is difficult to determine an optimum value for Φ unambiguously. It is expected from the calculations that the optimal angle Φ is neither 0° nor 90° and that rotation is nearly free. This is also consistent with the optimal CC bond length which is very close to the single-bond value.

Our calculations show that the fluorine 1,2 migration (shuttling motion) is in principle possible but highly unlikely because the activation energy is high and the saddle point lies only 40–50 kJ/mol below the dissociation limit into $F + C_2H_4$. The rotation around the CC axis is found to be nearly free and will probably reduce the A factor for the shuttling reaction. Furthermore, the decomposition of C_2H_4F into $H + C_2H_3F$ could be a competitive reaction to the shuttling motion. The activation energy is predicted in the range of the activation energy for the 1,2 migration; e.g., an MP2/6-31G* calculation of Schlegel et al.^{3,4} gives 183 kJ/mol, a value which would possibly be lower in a CI calculation.

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Theoretical Analysis of the Fluorescence and Excitation Spectra of *m*-Xylylene Diradicals

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The vibrational structure of fluorescence and fluorescence excitation spectra of the diradical mesitylenediyl is analyzed by quantum mechanical calculations. It is shown that most of the bands appearing in these spectra are of a_1 type and that the emission–excitation spectral asymmetry is due to interference between vibronically induced and symmetry-allowed transition moments associated with the totally symmetric mode $6a$. The b_2 modes that strongly couple T_1 and T_2 are shown to be scarcely active in inducing transition intensity since the T_0 – T_2 transition moment is small. A particularly large T_1 – T_2 coupling is found for ν_8 , and the potential along this mode acquires a double-minimum shape. Fluorescence and fluorescence excitation spectra of mesitylenediyl are successfully interpreted in terms of computed adiabatic frequencies and of displacement parameters of a_1 vibrations in $T_1(1A_1)$ and $T_2(2B_2)$ relative to $T_0(1B_2)$.

1. Introduction

Conjugate diradicals have two singly occupied orbitals that are degenerate or quasi-degenerate and extend over a common π -system. These compounds have low-energy excited states of both triplet and singlet spin multiplicity and have been shown to be the intermediates of many photochemical reactions. At the same time, the ground state of the diradicals is rich in energy, and thus, at room temperature and in fluid solutions, it is often unstable and highly reactive.

Many efforts have been devoted to the characterization of ground and lowest excited states of diradicals. Because of their short lifetimes, they can be studied, at room temperature, only by transient techniques.^{1–3} A convenient alternative procedure

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