

Study Of S_n2 Reaction Between Methylbromide And Fluoride Ion Using Quantum Mechanical Calculations

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I. Introduction

1.1 Computational Chemistry

Computational chemistry [1] is a branch of chemistry that uses the principles of computer science to assist in solving chemical problems. It uses the results of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. The programs used in computational chemistry are based on many different quantum chemical methods that solve the molecular Schrodinger equation associated with molecular Hamiltonian.

We use Ab-initio method for finding transition state of a bimolecular reaction. An Ab-initio method [2] is an approach to calculate energy and many other properties of molecule by solving Schrodinger equation. The simplest type of Ab-initio electronic structure calculation is the Hartree - Fock (HF) scheme, an extension of molecular orbital theory, in which the correlated electron-electron repulsion is not specifically taken into account, only its average effect is included in calculation.

Gaussian is a computational chemistry software program [3] which is used in this study. Starting from the basic laws of quantum mechanics, Gaussian predicts the energies, molecular structures and vibrational frequencies of molecular systems, along with numerous molecular properties derived these basic computation types. It can be used to study molecules and reactions under a wide range of conditions, including both stable species and compounds which are difficult or impossible to observe experimentally such as short lived intermediates and transition structures. Gaussian 03 versions are used in this study.

CHAPTER – 2

II. AB- Initio Method- An Overview

2.1 Introduction

The aim of Ab initio molecular orbital theory is to predict the properties of atoms and molecules. It is based on the fundamental laws of quantum mechanics [4, 5]. Different mathematical transformations and approximation techniques are necessary to solve the equations that build up this theory. We review this theory briefly.

2.2 The Schrodinger Equation

For an isolated N-electron atomic or molecular system within the Born-Oppenheimer approximation, the electronic Schrodinger equation is given by

$$\hat{H}_{elec} \Phi_{elec}(r) = E_{elec} \Phi_{elec}(r) \dots\dots\dots 2.1$$

where $E_{elec} = E_{elec}(\{R_A\})$ is the electronic energy, $\Phi_{elec} = \Phi_{elec}(\{r_i\}, \{R_A\})$, is the wave function which describes the motion of electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates, as does the electronic energy. By a parametric dependence we mean that, for different arrangements of the nuclei Φ_{elec} is a different function of the electronic coordinate. \hat{H}_{elec} Is the electronic Hamiltonian operator describing the motion of N electrons in the field of M point charges:

$$\hat{H}_{elec} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \dots\dots\dots 2.2$$

The total energy E_{tot} is the electronic energy E_{elec} including the nuclear repulsion energy according to the following equation:

$$E_{tot} = E_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \dots\dots\dots 2.3$$

2.3 The Hartree-Fock Approximation

The Hartree-Fock approximation [6, 7] is a mean field approximation, where an electron is thought to move in the average field due to all other electrons present in the system. On the basis of the variation theory, the lowest value of \bar{E} is approximated as E_0 identified as the electronic energy for the selected nuclear configuration.

$$E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle \dots\dots\dots 2.4$$

where $\psi_0 = |\chi_1, \chi_2, \dots, \chi_N\rangle$ is a single Slater determinant. By minimizing E_0 with respect to the spin orbitals, it is possible to derive Hartree-Fock equation, which is basically an eigenvalue equation of the type,

$$\hat{f}_i(i) \chi_i(x_i) = \epsilon_i \chi_i(x_i) \dots\dots\dots 2.5$$

where the $\hat{f}_i(i)$ is an effective one electron operator called the Fock operator [8] having the following form,

$$\hat{f}_i(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i) \dots\dots\dots 2.6$$

Here $v^{HF}(i)$ is the average potential experienced by the i-th electron due to the presence of other electrons in the system. The essence of the Hartree-Fock approximation [9] is to replace the complicated many-electron problem by one electron problem in which the electron-electron repulsion is treated in an average way. The Hartree-Fock potential, $v^{HF}(i)$, term depends on the spin orbital of other electrons i.e., the Fock operator depends on its own eigenfunctions. Thus Hartree-Fock equation is non-linear and has to be solved iteratively.

The Hartree-Fock calculations can be closed-shell calculations with all paired electrons or open shell calculations with some unpaired electrons. In closed-shell restricted Hartree-Fock (RHF) calculations [10] all the electrons are paired so that the spatial orbitals are doubly occupied. In unrestricted Hartree-Fock (UHF) calculations the orbitals need not be doubly occupied. The HF equations might be solved numerically according to the suggestion of Roothaan and Hall. A set of known spatial basis functions (for example, atomic orbital basis functions) is introduced and the unknown molecular orbitals are expanded in the linear expansion:

$$\psi_i = \sum_{\mu}^K C_{i\mu} \phi_{i\mu} \dots\dots\dots 2.7$$

The problem of calculating the HF molecular orbitals is then reduced to the problem of calculating a set of expansion coefficients. Substituting the above equation into the HF integrodifferential equation therefore gives $\mathbf{FC} = \mathbf{SC}\epsilon$ where \mathbf{F} , \mathbf{S} , \mathbf{C} and ϵ are Fock matrix, overlap matrix, square matrix of the expansion coefficients, and the diagonal matrix of the orbital energies ϵ_i , respectively.

2.4 Ab-initio Method

The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular Schrodinger equation associated with the molecular Hamiltonian. Methods that do not include any empirical or semi-empirical parameters in their equations-being derived directly from theoretical principles, with no inclusion of experimental data are called Ab-initio method [11]. This does not imply that the solution is an exact one; they are all approximate quantum mechanical calculations. It means that a particular approximation is rigorously defined on first principles (quantum theory) and then solved within an error margin that is qualitatively known beforehand. If numerical iterative methods have to be employed, the aim is to iterate until full machine accuracy is obtained. The simplest type of Ab-initio electronic structure calculation [12] is the Hartree-Fock (HF) scheme, an extension of molecular orbital theory, in which the correlated electron-electron repulsion is not specially taken into account; only its average effect is included in the calculation.

2.5 Gaussian 03

Gaussian 03 version in the Gaussian series of electronic structure program is used for this study. Gaussian 03[13,14] is used by chemists, chemical engineers, biochemists, physicists and others for research in established and emerging areas of chemical interest. Starting from the basic laws of quantum mechanics,

Gaussian predicts the energies, molecular structures, and vibrational frequencies of molecular systems, along with numerous molecular properties derived from these basic computation types.

III. Geometry Optimization

3.1 Introduction

The geometry of a molecule determines many of its physical and chemical properties. This is why it is very important that we understand the geometry of a molecule when running computations. In computational chemistry we are specifically concerned with optimizing bond angles (degrees), bond lengths (angstroms) and dihedral angles (degrees). Geometry optimization [15, 16] is either an energy minimization or a transition state optimization. The aim of geometry optimization is to generate the lowest energy structure of a molecule from an arbitrary starting state. The way the energy of a molecular system varies with small changes in its structure is specified by its potential energy surface. A potential energy surface is a mathematical relationship linking molecular structure and the resultant energy. For a diatomic molecule, it is a two-dimensional plot with the internuclear separation on the X-axis and the energy at that bond distance on the Y-axis, producing a curve. For larger systems, the surface has as many dimensions as there are degrees of freedom within the molecule.

3.2 Potential Energy Surface (PES)

Potential energy surface [17, 18] is the potential interaction energy of nuclei in a molecular system. It is a function of the nuclei internal coordinates (bonds, angles and dihedral angles). If a molecule has N atoms, it has three degrees of freedom for translational motions of the whole molecule and two or three overall rotational motions if it has a linear or non-linear structure, respectively. Thus the potential energy surface has a (3N-5) or (3N-6) dimensions. The simplest potential energy surface is the potential curve of a diatomic molecule that is a function of only the bond distance.

There are minima on the potential surface. A minimum is the bottom of a valley on the potential surface. From such a point, motion in any direction- a physical metaphor corresponding to changing the structure slightly- leads to a higher energy. A minimum can be a local minimum, meaning that it is the lowest point in some limited region of the potential surface, or it can be the global minimum, the lowest energy point anywhere on the potential surface. Minima occur at equilibrium structures for the system, with different minima corresponding to different conformations or structural isomers in the case of single molecules, or reactant and product molecules in the case of multicomponent systems.

Peaks and ridges correspond to maxima on the potential energy surface. A peak is a maximum in all directions. A point which is a maximum in one direction and a minimum in the other is called a saddle point. For example, the saddle point is a minimum along its ridge and a maximum along the path connecting minima on either side of the ridge. A saddle point corresponds to a transition structure connecting the two equilibrium structures.

Potential energy surface is calculated by solving the Schrodinger equation using the Born-Oppenheimer approximation which assumes the electron motions can be separated from the nuclear motions for a large number of geometrical structures. Since the Schrodinger equation can only be solved approximately for multi-electron systems, depending on the level of approximation (method/basis set) used, locations of these stationary points (minimum or transition state) may vary from their 'true' structures.

3.3 Locating Minima

Geometry optimizations usually attempt to locate minima on potential energy surface, thereby predicting equilibrium structures of molecular systems [19]. Optimizations can also locate transition structures. Optimizations to minima are called minimizations.

At both minima and saddle points the first derivative of the energy, known as the gradient, is zero. Since the gradient is the negative of the forces, the forces are also zero at such a point. A point on the potential energy surface where the forces are zero is called a stationary point. All successful optimization locate a stationary point, although not always the one that was intended.

A geometry optimization begins at the molecular structure specified as its input, and steps along the potential energy surface, it computes the energy and the gradient at that point, and then determines how far and in which direction to make the next step. The gradient indicates the direction along the surface in which the energy decreases most rapidly from the current point as well as the steepness of that slope

Most optimization algorithms also estimate or compute the value of the second derivative of the energy with respect to the molecular coordinates, updating the matrix of forces constants. These force constants specify the curvature of the surface at that point, which provides additional information useful for determining the next step.

An optimization is complete when it has converged; essentially, when the forces are zero.

3.4 Transition State

Transition state of a chemical reaction corresponds to a saddle point on the potential energy surface. Searching for a local maximum is more difficult than a local minimum. One needs to provide a rather good guess in order for the optimization procedure to converge. For this reason, finding the transition state for a chemical reaction is not always trivial particularly large molecular systems. Once the transition state is located or optimized, it must be confirmed by performing a vibrational analysis. A saddle point should have one imaginary frequency (often printed as negative value by many quantum chemistry programs) and its vibrational mode should correspond to the motion that connects the reactant and product.

3.5 Reaction Path

Reaction path has several names, Minimum Energy Path (MEP) or Intrinsic Reaction Coordinate (IRC), is the steepest descent path starting from the saddle point toward both side of the downhill direction. An IRC calculation [20, 21] starts at the saddle point and follows the path in both directions from the transition state, optimizing the geometry of the molecular system at each point along the path. In this way, an IRC calculation definitely connects two minima on the PES by a path which passes through the transition between them.

When studying a reaction, the reaction path connects the reactants and the products through the transition state. Note that two minima on the PES may have more than one reaction path connecting them, corresponding to different transition state structures through which the reaction passes. From this point on, we will use the term reaction path to designate the intrinsic reaction path predicted by the IRC procedure, which can be qualitatively thought of as the lowest energy path, in mass-weighted coordinates, which passes through that saddle point.

Reaction path computations allow you to verify that a given transition structure actually connects the starting and ending structures that you think it does. Once this fact is confirmed, you can then go on to compute activation energy for the reaction by comparing the (zero-point corrected) energy of the reactants and the transition state.

IV. S_N2 Reaction

4.1 Introduction

The S_N2 reaction (also known as bimolecular nucleophilic substitution) is a type of nucleophilic substitution, where a lone pair from a nucleophilic attacks an electron deficient electrophilic centre and bonds to it, expelling another group called a leaving group. Thus the incoming group replaces the leaving group in one step. Since two reacting species are involved in the slow, rate determining step of the reaction, this leads to the name bimolecular nucleophilic substitution, or S_N2 [22]. Among inorganic chemist the S_N2 reaction is often known as the interchange mechanism.

4.2 Reaction mechanism

The reaction most often occurs at an aliphatic sp^3 carbon centre with an electronegative, stable leaving group attached to it-'X'-frequently a halide atom. The breaking of C-X bond and the formation of the new C-Nu bond occur simultaneously to form a transition state in which the carbon under nucleophilic attack is pentacoordinate, and approximately sp^2 hybridized. The nucleophile attacks the carbon at 180° to the leaving group, since this provides the best overlap between the nucleophile's lone pair and the C-X σ^* anti-bonding orbital. The leaving group is then pushed off the opposite side and the product is formed.

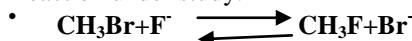
If the substrate under nucleophilic attack is chiral, this can lead, although not necessarily, to an inversion of stereo chemistry, called the Walden inversion.

In this study, the attack of F^- (the nucleophile) on methyl bromide (the electrophile) results in methyl fluoride with bromide ejected as the leaving group. S_N2 attack occurs if the backside route of attack is not sterically hindered by substituents on the substrate. Therefore, this mechanism usually occurs at an unhindered primary carbon centre. If there is steric crowding on the substrate near the leaving group, such as at a tertiary carbon centre, the substitution will involve an S_N1 rather than S_N2 mechanism.

V. Experimental Methods

5.1 Introduction

Reaction under study:



This study requires the following calculations:

- 1) Optimization of reactants and products
- 2) Two geometry optimizations to find the intermediate minima

- 3) An optimization of the transition state
- 4) A frequency job for the transition state

5.2 Input for geometry optimization

The Opt keyword in the route section request optimization, using the basis set, 6-31G (d). In Gaussian, the molecule specification for a geometry optimization can be given in any format desired. This study requires geometry optimization of reactants, products, transition structure and also two geometry optimizations to find the intermediate minima.

5.3 Input for frequency jobs

The Freq keyword in the route section requests a frequency job, using the basis set. The frequency calculations are valid only at the stationary points on the potential energy surface. Thus frequency calculation should be performed on optimized structures. So it is necessary to run a geometry optimization prior to doing a frequency calculation. The most convenient way of ensuring this is to include both Opt and Freq in the route section of the job, which request a geometry optimization followed immediately by a frequency calculation. Alternatively, one can give an optimized geometry as the molecule specification section for a stand-alone frequency job. A frequency job must the same theoretical model and basis set as produced in the optimized geometry. Frequencies computed with a different basis set or procedures have no validity.

Molecular frequencies depend on the second derivative of the energy with respect to the nuclear positions. Frequency calculations will determine the nature of a stationary point found by a geometry optimization. Geometry optimization converges to a structure on the PES where the forces on the system are essentially zero. The final structure may correspond to a minimum on the PES, or it may represent a saddle point. First order saddle points which are maximum in one direction and a minimum in all other orthogonal directions correspond to transition state structures linking two minima. Ordinary transition state structures are characterized by one imaginary frequency since they are first order saddle points.

Saddle points always connect two minima on the PES, but these minima may not be the reactants and products of interest. To confirm the existence of true transition state we perform IRC calculation. An IRC calculation begins at a transition structure and steps along the reaction path a fixed number of times in each direction, towards the two minima that it connects.

5.4 Reactants at infinite distance

CH_3Br and F^- are the reactants under study. CH_3Br and F^- are optimized to find the minimum energy structures. Input is given in the appendix A and B respectively. CH_3Br has C_{3v} symmetry. In this molecule all the three C-H bonds are same. In order to maintain the symmetry we use a “dummy atom, X” to specify the structure. The same value rh for all C-H bonds distance and ah for all H-C-H bond angles insists that the symmetry is maintained during the reaction.

5.5 Reactant system in the minimum energy state

In the initial stage both reactants are at infinite distance. When they approach each other, the energy of the whole system decreases and reach a minimum energy state of the reactant system. When they approach further the energy of the system increases. We have to optimize the $\text{CH}_3\text{Br} \cdots \text{F}^-$ system to get the minimum energy state. The input for this is given in the appendix C. Here Br-C-F bond angle is taken to be 180° to ensure that F^- approaches from opposite side of leaving group and also linear to Br group. Here also we use same variables for all C-H bond lengths and H-C-H bond angles respectively.

5.6 Products at infinite distance

CH_3F and Br^- are the products present in the reaction under study. Optimization process is done for both of them individually. That means they are far apart without any interactions. Input for products is given in the appendix D. In this case also a dummy atom is used to maintain symmetry of the molecule.

5.7 Product system in the minimum energy state

As Br^- moves apart and F^- come closer to C atom of CH_3Br , the energy of the system decreases and reaches a minimum energy state. As F^- approach further the energy of the system increases. Input for this is given in appendix E. Here also a dummy atom is used.

5.8 Transition state (TS)

TS correspond to the highest point in the minimum energy path. Input of TS is given in the appendix F. Existence of TS is verified by IRC calculation. Z-matrix is given in such a way that Br, C, F lie in a straight line.

VI. Results And Discussions

As mentioned in chapter 5, geometric optimization has been performed on various molecules. Information obtained from the output data are the following.

6.1 Reactants

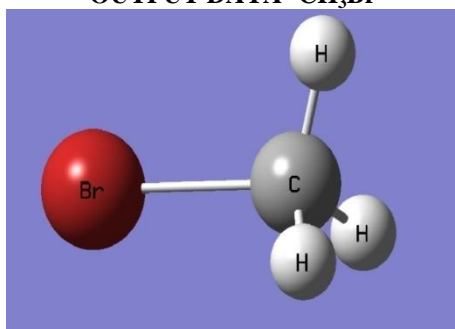
Total energy of CH_3Br is found as a result of optimization and it is about -2609.50067853 Hartrees. Changes in the parameters have observed. The optimized C-Br bond length is equal to 1.9477 Å and optimized H-C-Br bond angle equal to 111.1908° . Total energy of F^- equal to -99.35048197 Hartrees. Total energy of the reactant system at infinite distance is equal to -2708.89114847 Hartrees.

6.2 Minima I

Total energy of the system is found to be equal to -2708.89114847 Hartrees. Minima I correspond to a structure in which C-Br distance is equal to 2.0107 Å and C-F distance is equal 1.1337 Å. The optimized H-C-Br bond angle equal to 111.0823° .

After these findings we compared the energies of reactant system and minima I. Sum of energies of CH_3Br and F^- is equal to -2708.89114847 Hartrees. Energy of minima I is equal to -2708.93615459 Hartrees. Minima I has 0.04500615 Hartrees of energy less than the reactant system.

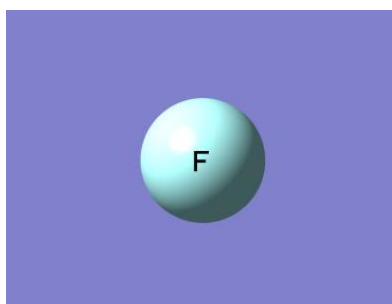
OUTPUT DATA- CH_3Br



HF		= -2609.50067850 Hartree
Zero point correction		= 0.039988 Hartree
Total energy		= -2609.5406665 Hartree

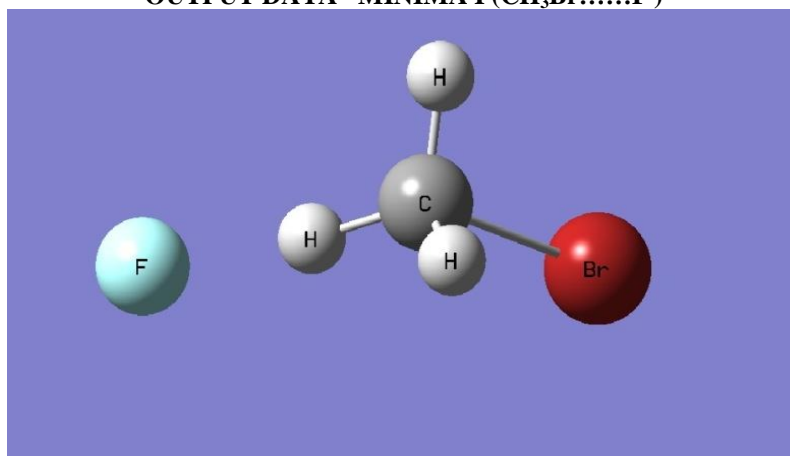
PARAMETER	INPUT	OUTPUT
Bond length C-Br(Å)	3.5	1.9477
Bond angle H-C-Br(Å)	109.8	111.1908

OUTPUT DATA - F^-



HF		= -99.35048197 Hartree
Zero point correction		= 0.0000 Hartree
Total energy		= -99.35048197 Hartree

OUTPUT DATA –MINIMA I (CH₃Br.....F⁻)



HF = -2708.89670659 Hartree
 Zero point correction = 0.039448 Hartree
 Total energy = -2708.93615459 Hartree

PARAMETER	INPUT	OUTPUT
Bond length C-Br(Å)	1.5	2.0107
Bond length C-F(Å)	1.9	1.1337
Bond angle H-C-Br (°)	109.5	111.0823

Comparison

SYSTEM	TOTAL ENERGY (Hartrees)
CH ₃ Br	-2609.540665
F	-99.35048197
CH ₃ Br+F	-2708.89114847
MINIMA I	-2708.93615459

6.3 Products

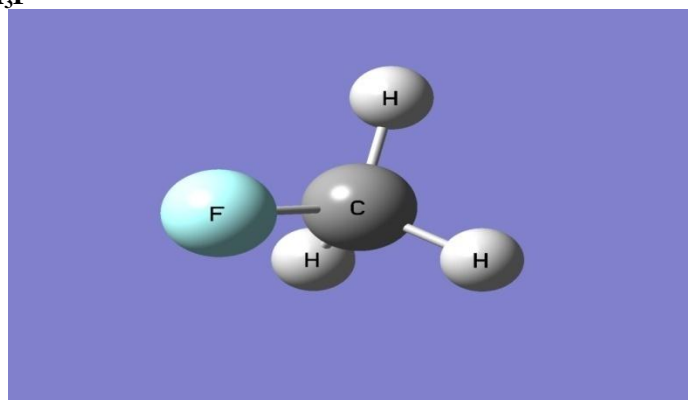
Total energy of CH₃F is found to be equal to -139.0770542 Hartrees. After optimization the C-F bond distance equal to 1.3643 Å and H-C-F bond angle 109.0975°. Total energy of Br⁻ is equal to -2569.93750106 Hartrees. Total energy of product system is equal to -2709.01455526 Hartrees.

6.4 Minima II

Total energy of this system is equal to -2708.03105516 Hartrees. Minima II corresponds to an structure in which C-Br bond distance is equal to 1.3643 Å and C-F bond distance equal to 1.0819 Å. The optimized bond angles H-C-Br is equal to 109.0975°

Sum of the energies of product system is equal to -2709.01455526 Hartrees. Energy of minima II is equal to -2708.83873898 Hartrees. From this it's clear that minima II have 0.17581628 Hartrees of energies less than product system.

OUTPUT DATA - CH₃F



HF = -139.03461520 Hartree
 Zero point correction = 0.042439 Hartree
 Total energy = -139.0770542 Hartree

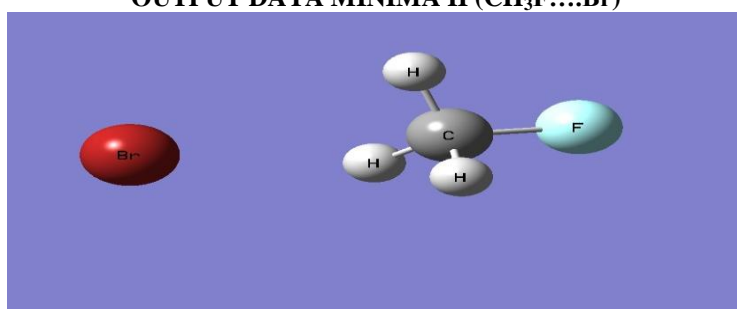
PARAMETER	INPUT	OUTPUT
Bond length C-F (Å)	1.5	1.3643
Bond angle H-C-F (°)	109.8	109.0975

OUTPUT DATA - Br⁻



HF = -2569.93750106 Hartree
 Zero point correction = 0.000 Hartree
 Total energy = -2569.93750106 Hartree

OUTPUT DATA MINIMA II (CH₃F...Br)



HF = -2708.98806716 Hartree
 Zero point correction = 0.042988 Hartree
 Total energy = -2709.03105516 Hartree

PARAMETER	INPUT	OUTPUT
Bond length C-F(Å)	1.7	1.0819
Bond length C-Br (Å)	1.9	1.3643
Bond angle	70.5	109.0975

Comparison

SYSTEM	TOTAL ENERGY (Hartrees)
CH ₃ F	-139.0770542
Br ⁻	-2569.93750106
CH ₃ F+Br ⁻	-2709.01455526
MINIMA II	-2709.03105516

6.5 Transition state (TS)

Total energy of TS is equal to -2708.838739 Hartrees. We observe only one negative frequency by doing various frequency jobs. This ensures that the predicted is TS. IRC calculation is also done for TS structure, which shows that TS connects the two minima.

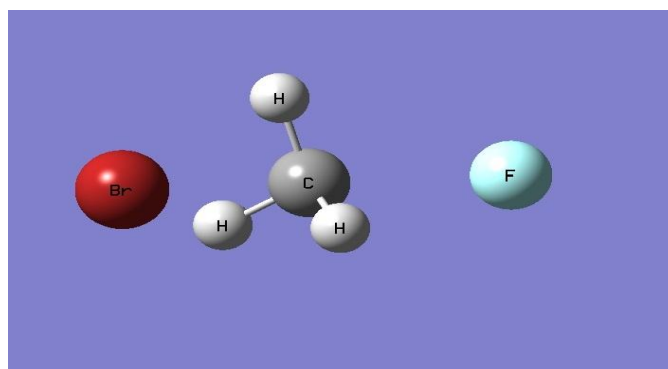
6.6 Activation energy

We have calculated the energy of reactants, products and TS. From this activation energy for the reaction under study is calculated.

For forward reaction it is about 0.052409 Hartrees. For backward reaction it is about 0.175816 Hartrees. From these values it is clear that forward reaction is more feasible than backward reaction.

Total energy of reactants, products, TS, minima I and minima II is given in the table. Using this potential energy surface is drawn.

OUTPUT DATA OF TRANSITION STATE

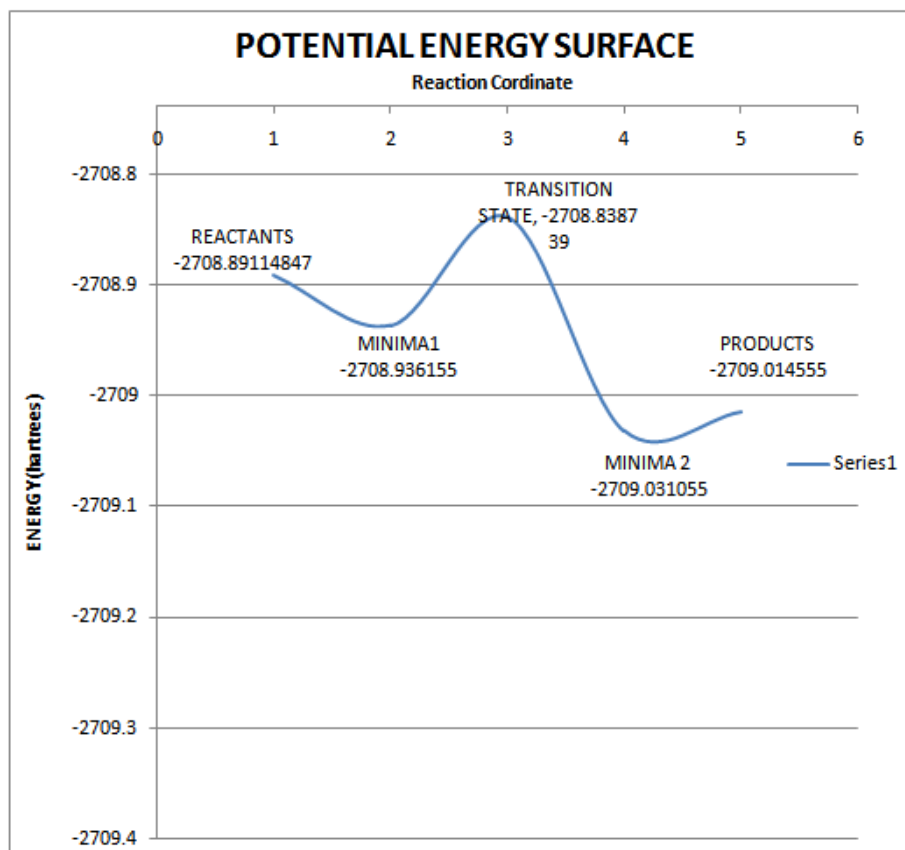


HF = -2708.80120498 Hartree
 Zero point correction = 0.037534 Hartree
 Total energy = -2708.838739 Hartree

TS-FREQUENCIES

-290.12
182.46
263.64
950.64
1209.26
1578.78
3110.51
3234.27

POTENTIAL ENERGY SURFACE



Activation Energy

SYSTEM;	TOTAL ENERGY(Hartrees)
CH ₃ Br+F	-2708.891148
CH ₃ F+Br ⁻	-2709.014555
TS	-2708.838739

1 Hartree=627.51kcal/mol

PARAMETER	FORWARD REACTION	BACKWARD REACTION
Activation energy	0.052409	0.175816

TOTAL ENERGY

SYSTEM	TOTAL ENERGY
REACTANTS	-2708.891148
MINIMA 1	-2708.936155
TRANSITION STATE	-2708.838739
MINIMA 2	-2709.031055
PRODUCTS	-2709.014555

VII. Conclusion

The frequency calculation confirms the existence of a transition structure, as well as providing zero point energy. The C-Br bond length increases as it proceeds in the forward direction along the reaction path, and this bond decrease in length in the reverse direction. C-F bond length changes in the complementary manner. A negative vibrational frequency shows the existence of true TS.

From the potential energy surface it is confirmed that the reaction follows S_N2 mechanism. Activation energy for forward reaction is less than that of backward reaction. So the feasible reaction is the formation of CH_3F from CH_3Br and F^- .

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APPENDIX A

CH₃Br

#T RHF/6-31G (d) Opt Freq Test

Methyl bromide

0 1

C

Br 1 3.5

H 1 1.1 2 109.8

H 1 1.1 2 109.8 3 120.0

H 1 1.1 2 109.8 3 -120.0

APPENDIX B

F⁻

#T RHF/6-31G(d) Opt Freq

F-

-1 1

F

APPENDIX C

MINIMA 1 CH₃Br.....F

#T RHF/6-31G (d) Opt Freq Test

Minima 1

-1 1

X

C 1 1.0

Br 2 1.5 1 90.0

F 1 1.9 2 90.0 3 180.0

H 2 1.1 3 109.5 1 0.0

H 2 1.1 3 109.5 1 120.0

H 2 1.1 3 109.5 1 -120.0

APPENDIX D

CH₃F

#T RHF/6-31G (d) Opt Freq Test

Methyl fluoride

0,1

C

F 1 1.5

H 1 1.1 2 109.8

H 1 1.1 2 109.8 3 120.0

H 1 1.1 2 109.8 3 -120.0

Br-

#T RHF/6-31G (d) Opt Freq Test

Bromide

-1 1

Br

APPENDIX E

MINIMA 2 CH₃F....Br

#T RHF/6-31G (d) Opt Freq Test

MINIMA2

-1 1

X

C 1 1.0

Br 2 1.9 1 90.0

F 2 1.7 1 90.0 3 180.0

H 2 1.1 3 70.5 1 0.0

H 2 1.1 3 70.5 1 120.0

H 2 1.1 3 70.5 1 -120.0

APPENDIX F

TRANSITION STATE

#T RHF/6-31G (d) Freq Test

Transition state

-1 1

X

C 1 1.0

Br 2 2.5 1 90.0

F 2 2.7 1 90.0 3 180.0

H 2 1.1 3 70.0 1 0.0

H 2 1.1 3 70.0 1 120.0

H 2 1.1 3 70.0 1 -120.0

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