

ABSTRACT:

The energetics of the stationary points of the gas-phase reactions $\text{CH}_3\text{X} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{X}^-$ (where $\text{X} = \text{F}, \text{Cl}, \text{CN}, \text{OH}, \text{SH}, \text{NH}_2$) have been computed in this project. The analysis of the computational output data led to the proper understanding of the following schemes:

1. Ascertaining the relative stability of the reactants and products using HF, DFT(B3LYP), and MP2 energies in conjugation with 6-31+G(d) basis set. Here, the reactants and products have been optimised using Gaussian 09W with the help of visualizers: Avogadro and Gauss View. The optimised energy, calculated with the different level of theories, helped to get an idea about the relative stability.
2. The relative stability denotes the enthalpy of the reaction. After we get the computation analyse for the enthalpy of the particular $\text{S}_{\text{N}}2$ reaction in gas phase, we compare with the experimental results obtained from previous works^[1].
3. The final net activation barrier for the forward and reverse reactions have been calculated by optimizing the transition state.

The reactant complexes fall into two groups, mostly electrostatic complexes (FCH_3 , F^-) and those with substantial covalent character ($\text{ClCH}_3\cdot\text{F}^-$, $\text{NCCH}_3\cdot\text{F}^-$, $\text{CH}_3\text{OH}\cdot\text{F}^-$, $\text{CH}_3\text{SH}\cdot\text{F}^-$, $\text{CH}_3\text{NH}_2\cdot\text{F}^-$) as observed with the help of the visualizers as mentioned. All of the product complexes are of the form $\text{FCH}_3\cdot\text{X}^-$ and are primarily electrostatic in nature. **All the topics discussed above has been studied and the observations have been noted down with illustrations and discussions as and when required.**

PART 1:

In a $\text{S}_{\text{N}}2$ reaction, out of the five stationary points^[1] we have analysed the energies of two of them. They are the corresponding ion-molecule complexes that we obtain by optimising the reactants and products. Generally, several geometries are possible for these types of structures. For the accomplishment for this particular project, we have begun our study by considering the linear backside attack, but while optimising the geometries we observed minimum structures of this type for only one of our studied six reactions. Some previous research suggested the linear backside attack and then computed for the corresponding stationary points, but they have not reported stability.

The potential energy surfaces have been examined in the methods of HF, MP2 and B3LYP using the diffused basis set 6-31+G(d) and we have arrived at geometry and energy optimised structures of the reactants and the products. The optimised structures that we obtained are the respective ion-molecules complexes of the reactants and the products for a particular reaction. We have noted down the respective optimised energies and then computed for the relative stability (E^0) for both the product and reactant pair for each reaction under this particular topic. Considering the general reaction to be studied : $\text{CH}_3\text{X} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{X}^-$ (where $\text{X} = \text{F}, \text{Cl}, \text{CN}, \text{OH}, \text{SH}, \text{NH}_2$), we have: $E^0_{\text{F,X}} = E(\text{CH}_3\text{F}) + E(\text{X}^-) - E(\text{CH}_3\text{X}) - E(\text{F}^-)$

This particular quantity(E^0) has been depicted in the following potential energy surface for a general $\text{S}_{\text{N}}2$ type reaction:

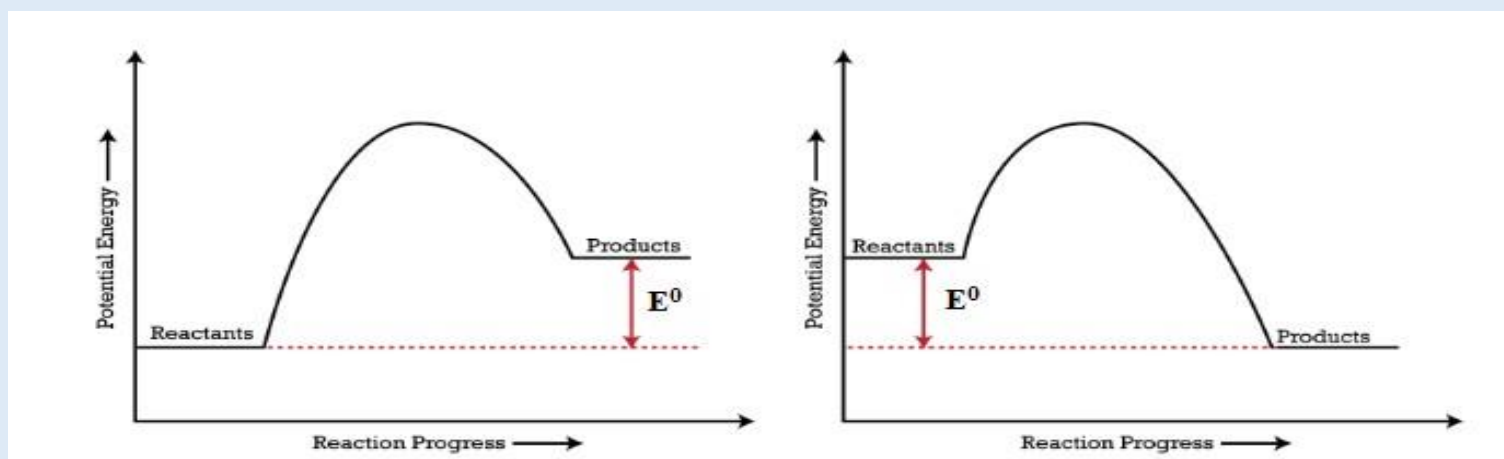


FIG:1

The value of E^0 , which is the difference in stabilisation energy between the products and the reactants, can be positive or negative depending on whether the reaction is **endothermic** or **exothermic**.

Considering the reaction $\text{CH}_3\text{F} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{F}^-$:

- The identity $\text{S}_{\text{N}}2$ reaction with F^- as both the nucleophile and a leaving group has been studied by optimising the structure of the reactants and products by employing methods HF, MP2 and B3LYP using the basis set 6-31+g(d). We have included the optimised structures, with the suitable geometric parameters, of the reactants and products of this reaction in Fig:2. As this is an identity reaction, the structure of the reactant and the product complexes are similar. The adducts that we get for this reaction are electrostatic in nature.
- Considering the energetics of this particular reaction, after computation, we obtained the energy of the reactant complex and the product complexes and got their relative stability in kcal/mole, which has been tabulated in Table:1.
- The relative stability that we got for this reaction is nearly 0 kcal/mole with the mentioned basis set but according to the results of previous works we can get a more precise value when we can include correlation factors in the basis set used and do the necessary computation.

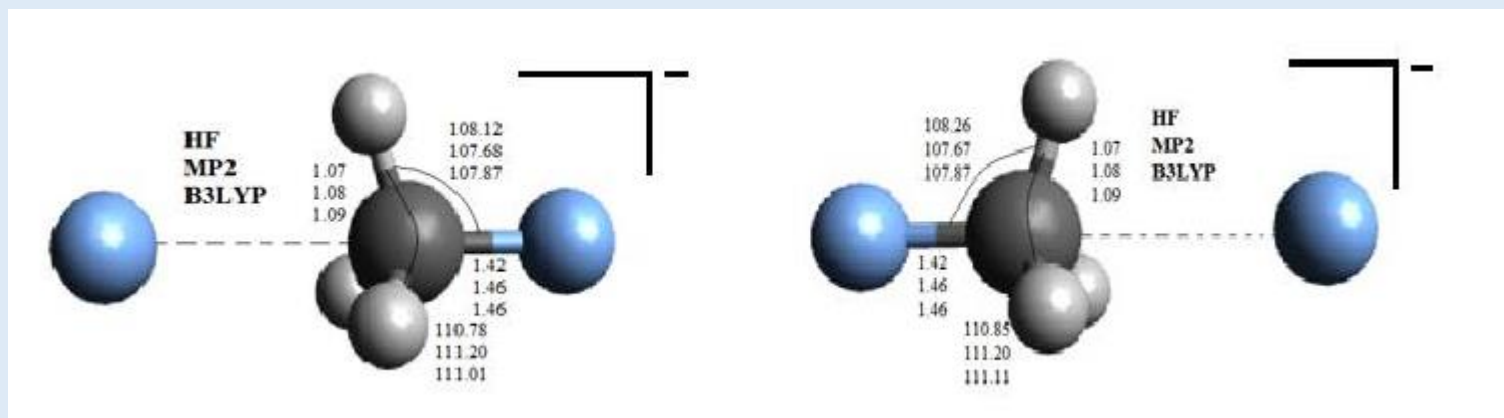


FIG:2 Geometries of the ion-molecule complex of reactants and products for the reaction $\text{CH}_3\text{F} + \text{F}^-$ using the 6-31+G(d) basis set. All bond distances are in Å and bond angles in degrees. The ion-molecule complexes have C_{3v} point group.

TABLE:1 The energetics of the reaction: $\text{CH}_3\text{F} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{F}^-$

	$E_{\text{reactants}}$ (in Hartree)	E_{products} (in Hartree)	$E^0_{\text{F,F}}$ (in Kcal/mol)
HF	238.483	238.483	0.003
MP2	238.999	238.999	1E-05
B3LYP	239.633	239.633	0.0001

The relative stability that we obtained in the various theories are positive, hence the reaction studied is **endothermic** in nature.

Considering the reaction $\text{CH}_3\text{Cl} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{Cl}^-$:

- This is the non-identity exchange reaction with Cl^- as the leaving group. We have included optimised structures, with suitable geometric parameters, of the reactants and products of this reaction in Fig:3. The structure of the reactant has some semi-covalent nature, due to H-bonding, with the F^- being aligned in the line of C-H whereas the structure of the product is electrostatic in nature. As per previous works ^[3,4,5], linear backside attack was assumed but they didn't talk about stability.
- Considering the energetics of this particular reaction, after computation, we obtained the energy of the reactant complex and the product complexes and got their relative stability in kcal/mole, which has been tabulated in Table:2.
- We observe disparity in the relative stabilities, when calculated in different theories, which could be due to the chosen basis set and proper density functionals that don't fit the requirement of the studied system. For this reaction, we arrived at more or less close results for the stabilities in the studied theories.

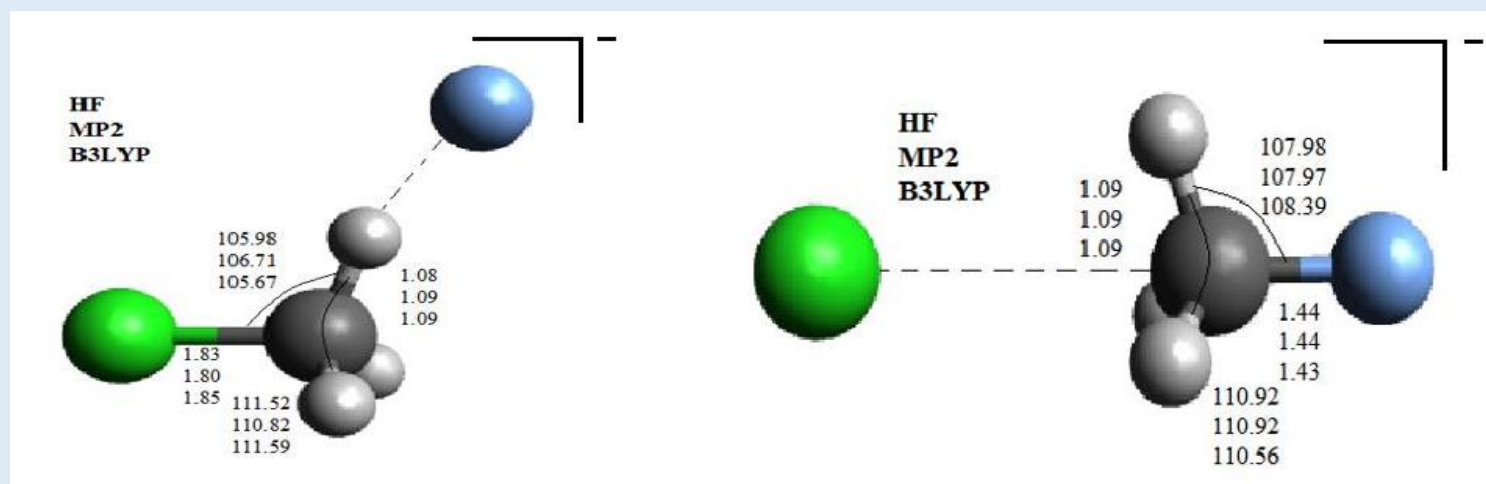


FIG:3 Geometries of the ion-molecule complex of reactants and products for the reaction $\text{CH}_3\text{Cl} + \text{F}^-$ using 6-31+G(d) basis set. All bond distances are in Å and bond angles in degrees. The ion-molecule complex of reactants have C_s point group while the products have C_{3v} point group.

TABLE:2 The energetics of the reaction: $\text{CH}_3\text{Cl} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{Cl}^-$

	E_{reactants} (in Hatrees)	E_{products} (in Hatrees)	E⁰_{F,Cl} (in Kcal/mol)
HF	-598.536	-598.595	-37.329
MP2	-599.005	-599.04	-21.606
B3LYP	-599.998	-600.039	-25.628

The relative stability that we obtained in the various theories are negative, hence the reaction studied is **exothermic** in nature.

Considering the reaction $\text{CH}_3\text{CN} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{CN}^-$:

- The reaction of Acetonitrile with the fluoride anion has been studied and we have included the optimised structures, with the suitable geometric parameters, of the reactants and products of this reaction in Fig:4. The structure of the reactant has some covalent nature whereas the structure of the product is electrostatic in nature. We observe that in the structure of the reactant, the fluoride ion is not on the C-C axis, instead is attached to a methyl hydrogen due to the presence of semi covalent hydrogen bond, that renders extra stability compared to its collinear moiety. As it was previously assumed^[3,4,5], to have a collinear backside attack, the computations reveal the existence of suitable semi-covalent character due to the presence of hydrogen bonding in the moiety which renders more stability than its electrostatic, collinear alternative structure as reported in the previous works.
- Considering the energetics of this particular reaction, after computation, we obtained the energy of the reactant complex and the product complexes and got their relative stability in kcal/mole, which has been tabulated in Table:3.
- In this reaction we observe some amount of disparity between the calculations done by HF compared to MP2 and B3LYP. Inclusion of proper diffused and polarisation basis function can yield better results as conclusive from previous works^[2].

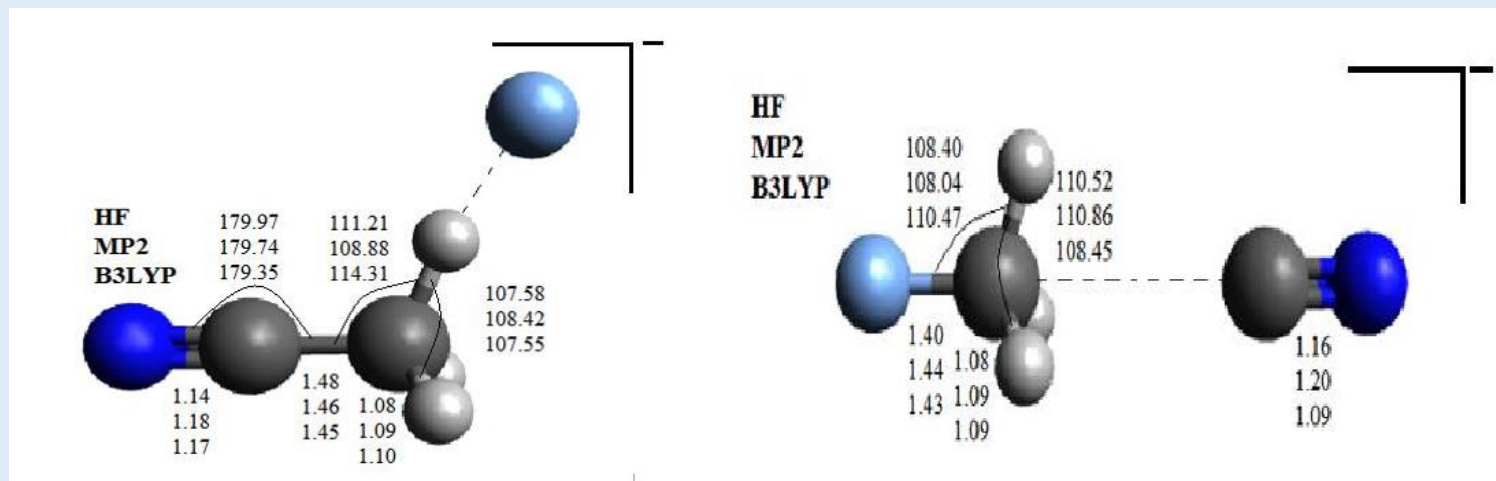


FIG:4 Geometries of the ion-molecule complex of reactants and products for the reaction $\text{CH}_3\text{CN} + \text{F}^-$ using the 6-31+G(d) basis set. All bond distances are in Å and bond angles in degrees. The ion-molecule complex of reactants are in C_s symmetry while the products are in C_{3v} symmetry.

TABLE:3 The energetics of the reaction: $\text{CH}_3\text{CN} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{CN}^-$

	$E_{\text{reactants}}$ (in Hartrees)	E_{products} (in Hartrees)	$E^0_{\text{F,CN}}$ (in Kcal/mol)
HF	231.377	231.371	3.567
MP2	232.003	231.971	20.165
B3LYP	-232.66	-232.63	19.279

The relative stability that we obtained in the various theories are negative, hence the reaction studied is **exothermic** in nature.

Considering the reaction $\text{CH}_3\text{OH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{OH}^-$:

- The reaction of methanol and the fluoride ion has been studied and we have included the optimised structures, with the suitable geometric parameters, of the reactants and products of this reaction in Fig:5. The reactant ion-molecule complex doesn't suggest a backside attack, hence, instead of being closer to the methyl carbon, fluoride is attracted to the more acidic hydroxyl hydrogen. This gives an extra stability to the moiety in compared to the other previously reported^[3,4,5], electrostatic, collinear structures. The product complex is electrostatic with the oxygen being pushed up slightly.
- Considering the energetics of this particular reaction, after computation, we obtained the energy of the reactant complex and the product complex and got their relative stability in kcal/mole, which has been tabulated in Table:4.
- Since this type of reactant includes a larger charge transfer effect and high order mixing due to the high fluoride affinity of methanol, higher order correlations become necessary for the computation making it inevitable to neglect error when performed with lower order basis set and therefore, error can appear and deviations are observed in the theory results.

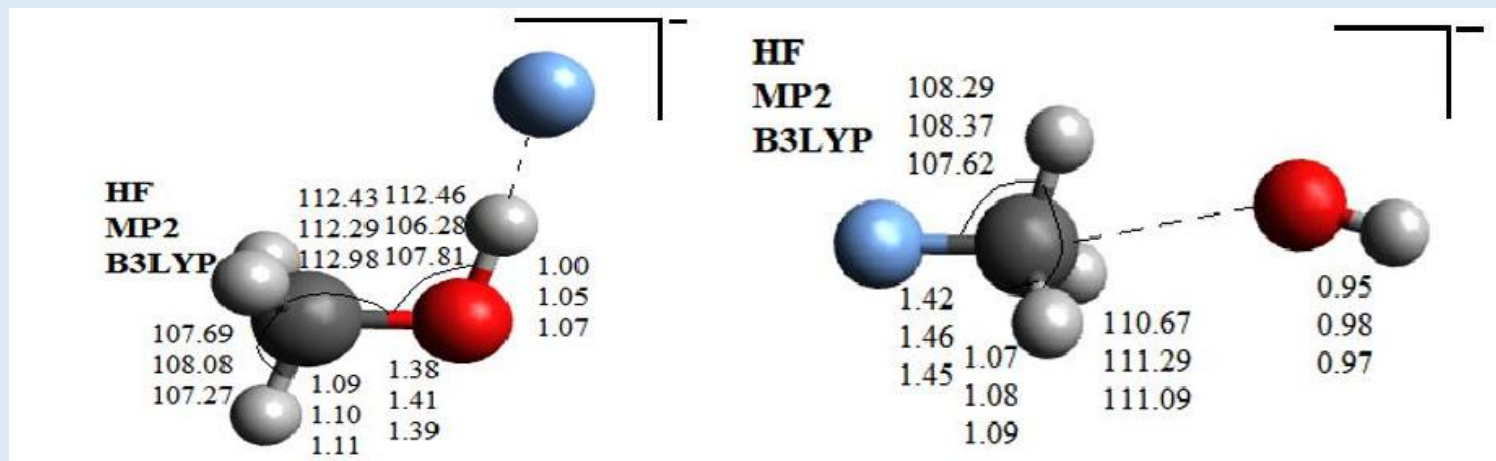


FIG:5 Geometries of the ion-molecule complex of reactants and products for the reaction $\text{CH}_3\text{OH} + \text{F}^-$ using the 6-31+G(d) basis set. All bond distances are in Å and bond angles in degrees. The ion-molecule complex of all structures are in C_s symmetry.

TABLE:4 The energetics of the reaction: $\text{CH}_3\text{OH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{OH}^-$

	E_{reactants} (in Hatrees)	E_{products} (in Hatrees)	E⁰_{F,OH} (in Kcal/mol)
HF	214.501	214.442	36.93
MP2	215.027	214.966	38.658
B3LYP	215.633	-215.57	39.455

The relative stability that we obtained in the various theories are positive, hence the reaction studied is **endothermic** in nature.

Considering the reaction $\text{CH}_3\text{SH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{SH}^-$:

- The reaction of methanethiol and fluoride has been studied and we have included the optimised structures, with suitable geometric parameters, of the reactants and products of this reaction in Fig:6. In this case we observe that, the H-F distance is very short and the S-H distance has been elongated in case of the reactant ion-molecule complex. This type of structure is a result of massive charge transfer effects. Some of the previous works^[3,4,5], considered backside collinear attacks but the proper optimisation resulted into such structure, which enhances stability for the particular complex. The product complex is electrostatic in nature with the sulphur being pushed up towards the unique methyl hydrogen.
- Considering the energetics of this particular reaction, after computation, we obtained the energy of the reactant complex and the product complexes and got their relative stability in kcal/mole, which has been tabulated in Table:5.
- Inclusions of higher correlated basis sets, same as in the case of methanol, can improve accuracy for predicting the energies in such moieties, due to the presence of charge transfer effects, between the various level of theories employed to study such type of reactions.

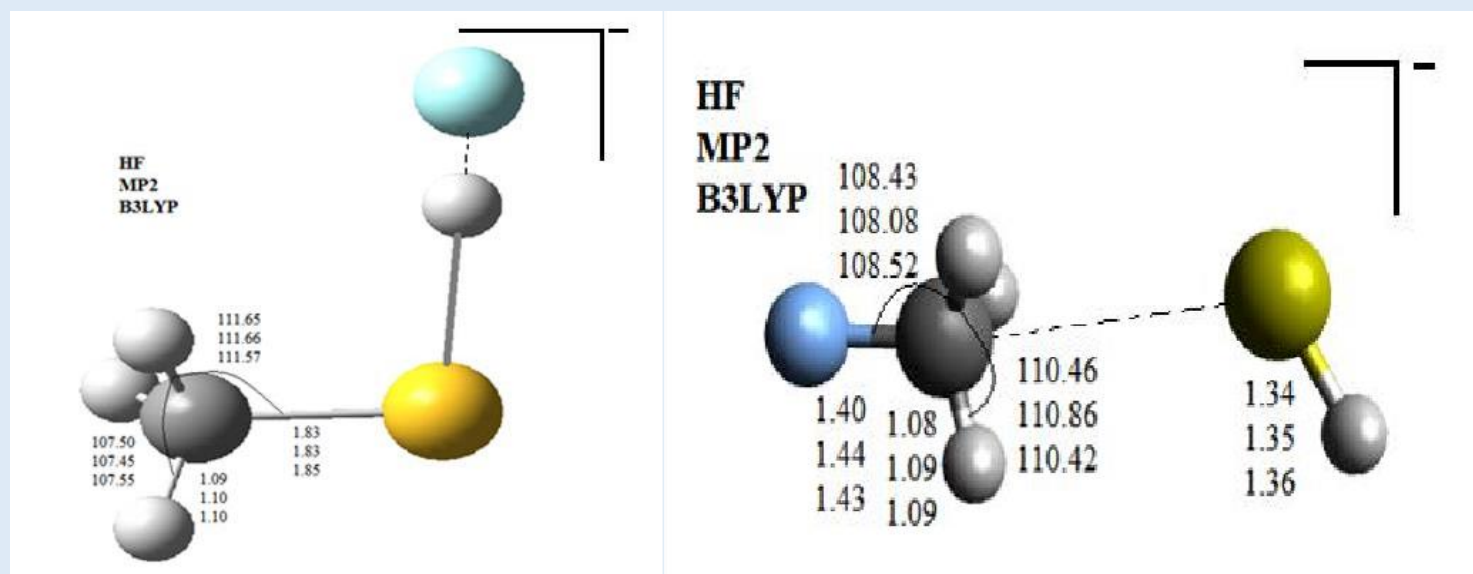


FIG:6 Geometries of the ion-molecule complex of reactants and products for the reaction $\text{CH}_3\text{OH} + \text{F}^-$ using the 6-31+G(d) basis set. All bond distances are in Å and bond angles in degrees. The ion-molecule complex of all structures are in C_s symmetry.

TABLE:5 The energetics of the reaction: $\text{CH}_3\text{SH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{SH}^-$

	E_{reactants} (in Hatrees)	E_{products} (in Hatrees)	E⁰_{F,OH} (in Kcal/mol)
HF	537.176	537.163	8.07
MP2	537.631	537.598	20.759
B3LYP	538.617	538.591	15.971

The relative stability that we obtained in the various theories are positive, hence the reaction studied is **endothermic** in nature.

Considering the reaction $\text{CH}_3\text{NH}_2 + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{NH}_2^-$:

- The reaction of methylamine and fluoride has been studied and we have included the optimised structures, with the suitable geometric parameters, of the reactants and products of this reaction in Fig:7. Instead of being in the H-C-N plane in CH_3NH_2 , the fluoride anion is connected to a single amine hydrogen. The H-F distance is somewhat longer than in the isolated HF, as observed from the optimised reactant complex, which indicates a modest charge transfer. Overall, the reactants show covalent nature due to hydrogen bonding to a single acidic proton. For the product ion-molecule complex, of electrostatic type, we observe that the amine group has been pushed up above the unique methyl hydrogen as we have seen for methanol and methanethiol cases. The linear backside attack model has not been established for the same previous reasons.
- Considering the energetics of this particular reaction, after computation, we obtained the energy of the reactant complex and the product complexes and got their relative stability in kcal/mole, which has been tabulated in Table:5.
- Similar to methanol and methanethiol reactions, this reaction also need to be studied under larger correlated basis sets to increase accuracy of results for the same reasons.

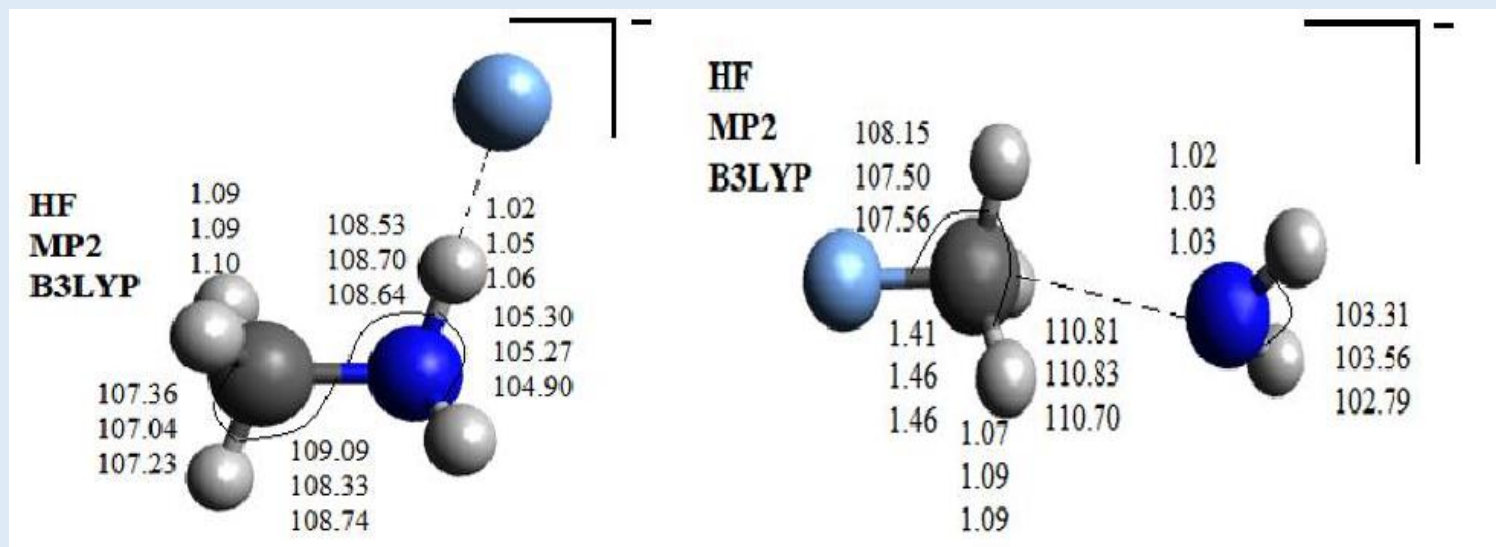


FIG:7 Geometries of the ion-molecule complex of reactants and products for the reaction $\text{CH}_3\text{NH}_2 + \text{F}^-$ using the 6-31+G(d) basis set. All bond distances are in Å and bond angles in degrees. . The ion-molecule complex of reactants is in C_1 symmetry while that of products is in C_{3v} symmetry.

TABLE:6 The energetics of the reaction: $\text{CH}_3\text{NH}_2 + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{NH}_2^-$:

	E_{reactants} (in Hatrees)	E_{products} (in Hatrees)	E⁰_{F,OH} (in Kcal/mol)
HF	194.656	194.582	46.15
MP2	195.166	195.085	50.767
B3LYP	195.749	195.673	47.909

The relative stability that we obtained in the various theories are positive, hence the reaction studied is **endothermic** in nature.

PART 2:

In this following section, we have tried to draw a comparison and analyse the theoretically computed results of Part- 1 with the experimental gas phase S_N2 reaction data obtained for these reactions from previous works^[1]. We have basically calculated the deviations of theoretically computed relative stabilities of the reactants and the products from the experimental results and the entire result has been tabulated in Table 5.

TABLE:7 Comparison of experimental $E_{F,X}^0$ evaluated with different theoretical methods:

	HF 6-31+G(d)		MP2/ 6-31+G(d)		B3LYP/ 6-31+G(d)		$E_{F,X}^0$ (Experimental)
X=	E^0(HF)	ΔE^0(HF)	E^0(MP2)	ΔE^0(MP2)	E^0(B3LYP)	ΔE^0(B3LYP)	
F	0	0	0	0	0	0	0
Cl	-37.33	6.13	-21.61	9.59	-25.63	5.57	-31.2
CN	3.57	1.43	20.17	15.17	19.28	14.28	5
OH	36.93	17.23	38.66	18.96	39.46	19.76	19.7
SH	8.07	22.77	20.76	35.46	15.97	30.67	-14.7
NH₂	46.15	8.65	50.77	13.27	47.91	10.41	37.5
Avg. ΔE^0	11.242		18.49		16.138		

Where, ΔE^0 = the absolute deviation between the theoretically computed relative stability of the reactants and the products, and the experimental results as cited by previous experimental works.

All values are in **kcal mol⁻¹** units.

- The statistical treatment of the energetics as tabulated in Table:5 reveals the largest disparity from the computed results in MP2/6-31+G(d) level of theory with the average deviation as 18.49 kcal/mol. Whereas we get better results with B3LYP and HF level of theories, where the average deviations came out to be 16.138 and 11.242 kcal/mol respectively. For this theoretical method that we employed to study these reactions, we can tell that MP2 is least favoured with the greatest scatter about E^0 (Experimental) data. HF gives the least deviations followed by B3LYP.
- One thing we observe in the table is that, for the reaction $\text{CH}_3\text{SH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{SH}^-$, the experimental results reveal the reaction to be exothermic but in our case we get endothermic values which indicate a total fallacy in our computed results and include large deviation from experimental data.
- The reaction moieties, that we have studied while calculating the relative energies, are anionic, more diffused with the presence of charge transfer effects and higher order mixing of electron densities. These systems can be well described by density functionals which are long range corrected functions with the inclusion of proper correlated, diffused and polarised basis sets. As we have seen in previous works^[2], the use of methods like CCSD(T) in conjugation with TZ2Pf+dif and aug-cc-pVTZ gave very good results and considered as highly correlated abinitio benchmarks for DFT assessment with functionals like B3LYP, BLYP, and BP86 variants, in conjunction with double and triple ζ basis sets, which concluded that the DFT functionals are not that effective in giving accurate results for the system studied in comparison with the coupled clusters theories and concluded considerable deviations from those treatments. Such coupled cluster treatments have not been employed in the project. As a result, we didn't arrive at very consistent data fitting the experimental results.
- We always expect DFT methods to be giving best results, but in this case we don't see that, perhaps the reasons lie on B3LYP which is not that kind of functional to fit the requirements of the studied system and we get better results for HF than DFT analyses. Perhaps, for the same reasons MP2 also failed to produce good results.
- For example, considering one research work^[6], though very different from our study tells about the failure of DFT treatment. According to the work, in [1.1.1] propellane, the distance between the inverted carbons (C_i) are constantly underestimated by density functionals especially by M06-2X. The possible reason being the overestimation of medium range correlation between the electron densities outside the central C-C axis. This observation is in line with the fact that M06-2X which was parametrized to include medium range correlations show the least bond length among all the DFT functional (B3LYP and B3PW91).
- This gives an insight to the fact that DFT analyses are best when proper functionals are applied system specifically, to reach its level of accuracy which would otherwise fail.

PART 3:

In this section, we show a visualised representation of the various reactions pathway that are being discussed, in the form of an intrinsic reaction coordinate (IRC) pathway, showing the forward and backward reaction barrier at MP2/6-31(+) G(d) level of theory ; this time by calculating the optimised energy of the transition state for the reactions.

The following are the IRC pathways along with the forward and backward reaction barrier:

- For the reaction $\text{CH}_3\text{F} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{F}^-$,

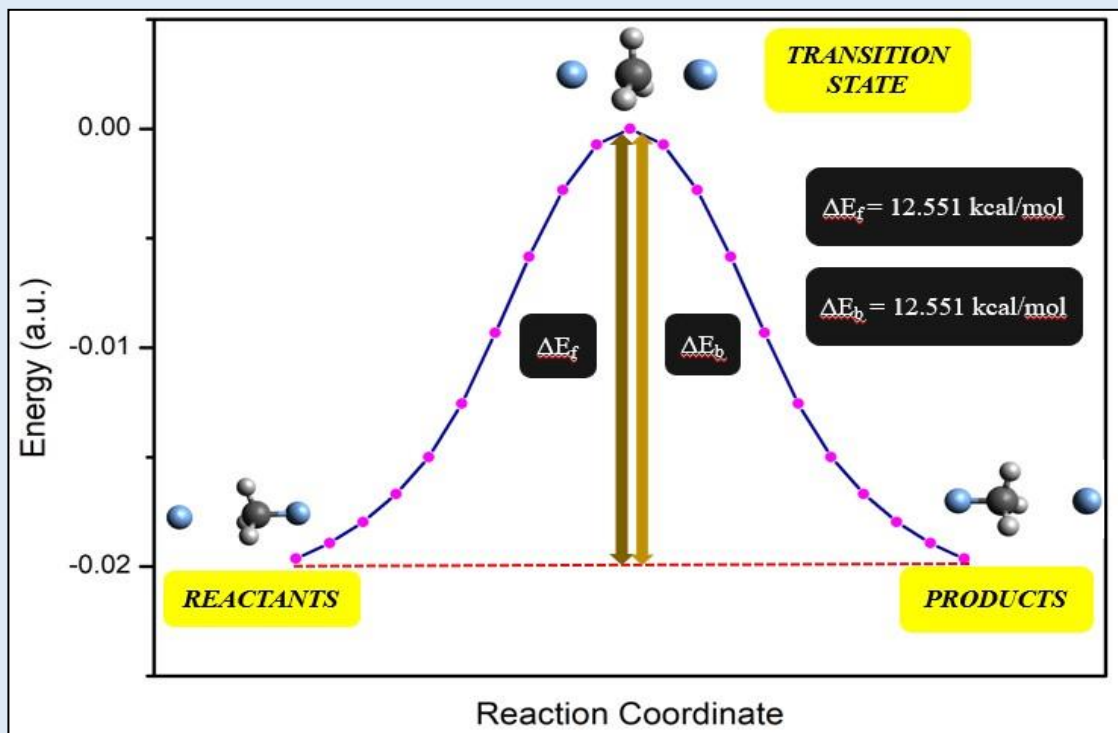


FIG:7

- For the reaction $\text{CH}_3\text{Cl} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{Cl}^-$,

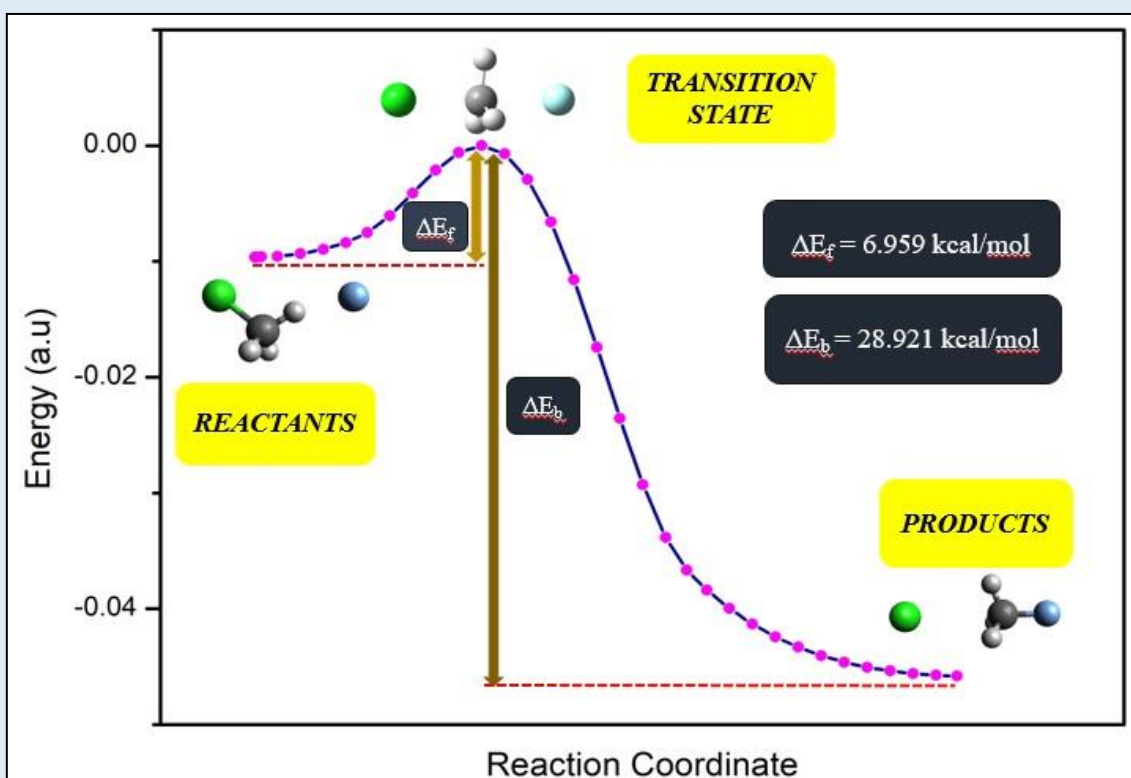


FIG:8

- For the reaction $\text{CH}_3\text{CN} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{CN}^-$,

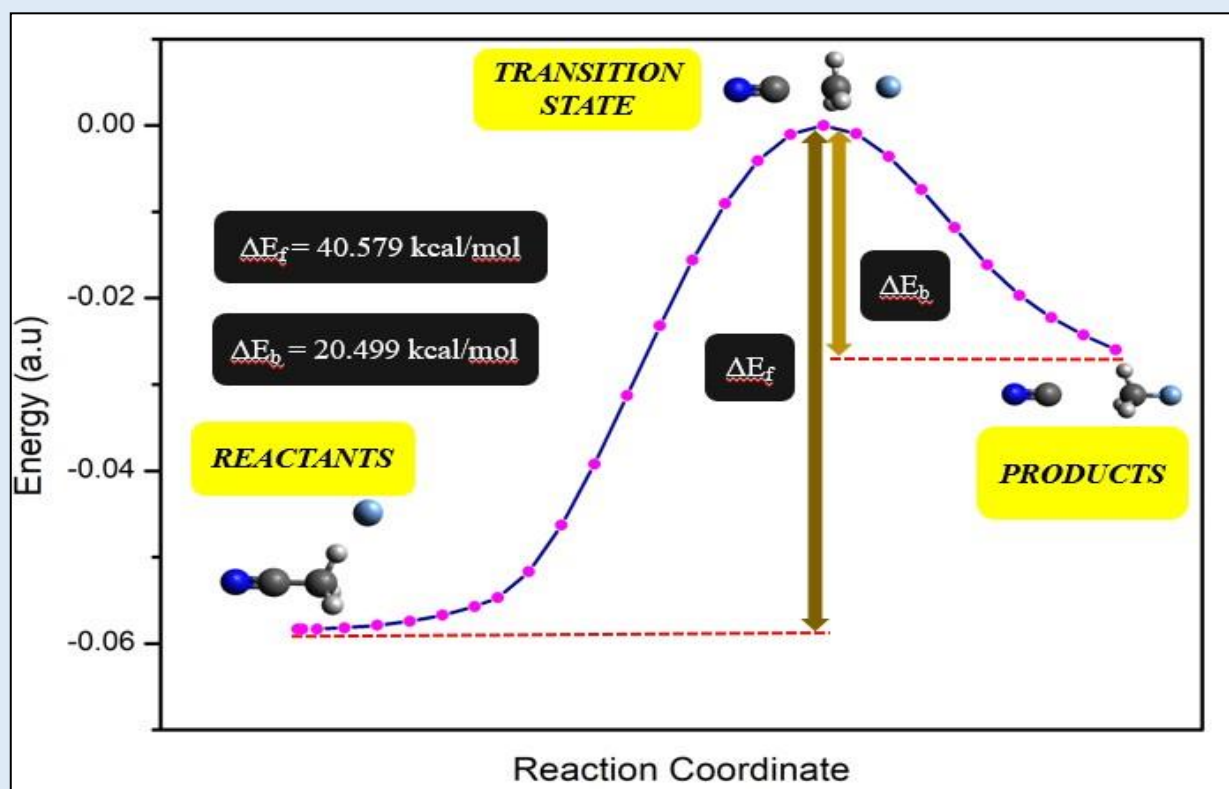


FIG:9

- For the reaction $\text{CH}_3\text{OH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{OH}^-$,

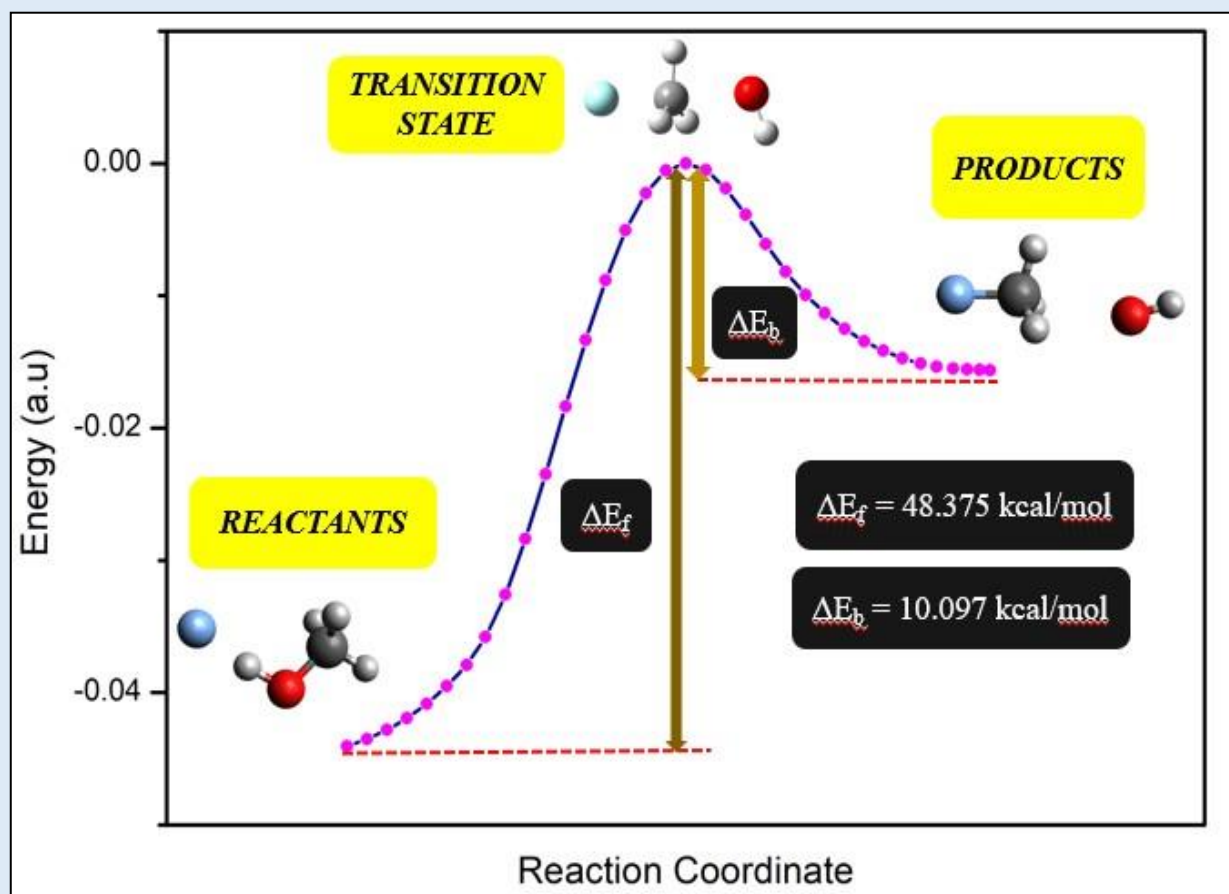


FIG:10

- For the reaction $\text{CH}_3\text{SH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{SH}^-$,

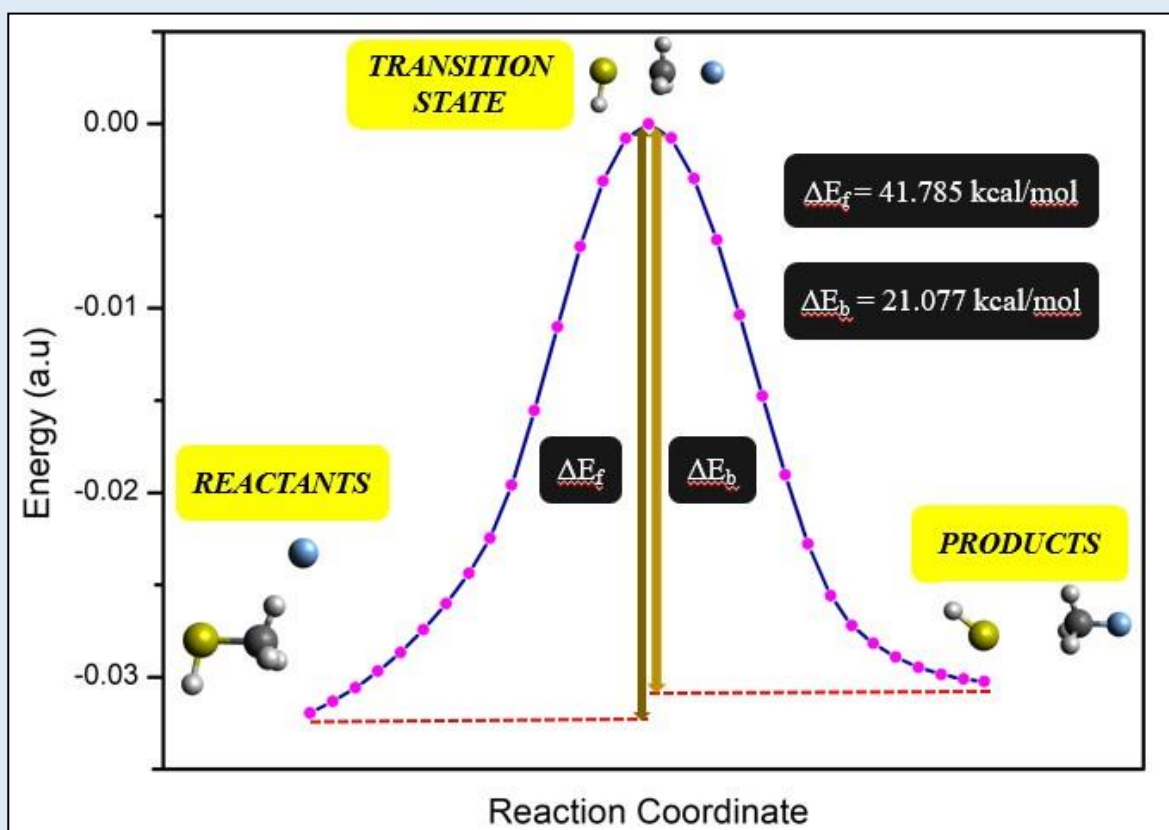


FIG:11

- For the reaction $\text{CH}_3\text{SH} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{SH}^-$,

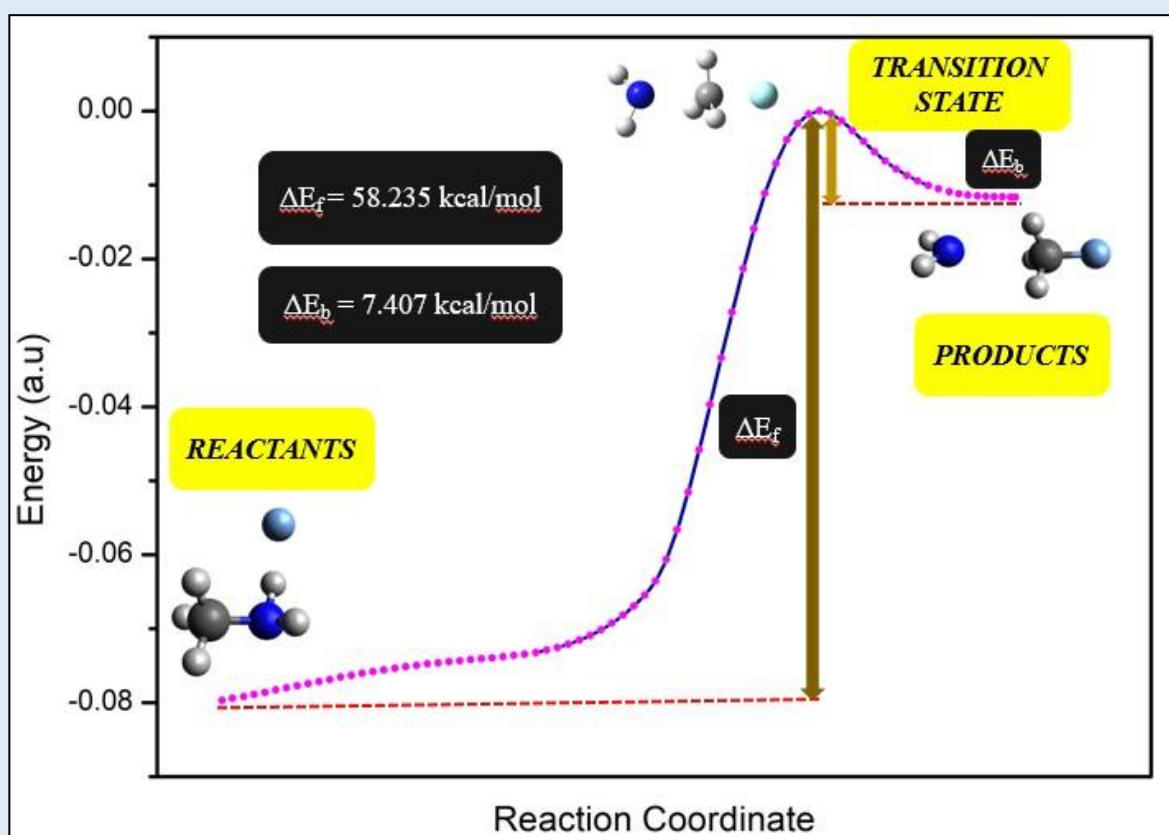


FIG:12

- For getting the IRC pathway, QST3 method was employed wherein, along with the approximate structure of transition state (TS) (optimised using semi-empirical methods for more accuracy; here PM3 was used), the optimised structure of the reactant as well as product was used to arrive at the optimised structure of transition state. The check point file (.chk file) generated in this calculation was used as the check point files for both forward and backward IRC calculation thereby arriving at the combined (forward and backward) IRC pathway for the reactions as shown above.
- The forward and backward barrier energies shown in each of the graphs were calculated as the difference between the optimised energy of transition state with that of the optimised energy of reactant and product respectively. The relative energy of the reactant and product obtained in IRC calculation are not taken because, the reactants and products in the calculation doesn't reach the actual minima (the stabilised structures of the complex pairs) where they reside everytime as the SCF cycles don't converge rigourously (which is again a problem for the basis set chosen for a particular system and the theories applied to calculate such reaction pathways) and the structure optimisations get arrested in a particular local minima as a result of which the threshold obtained in the case of IRC is not as accurate as that done by a suitable computational method for reaching the minima energy of the complex pairs of the reaction. The problem can be overcome by choosing a best fitting basis set of the studied system as discussed earlier.
- All optimisation have been done using the Gaussian 09W software^[7]. Avogadro^[8] and Gauss View^[9] have been used for visualising the molecules and Origin 8.5 have been used for drawing the graphs.

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