

Ab initio calculations of the potential energy surface for the reaction $N(^2D) + CH_3F$

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Abstract

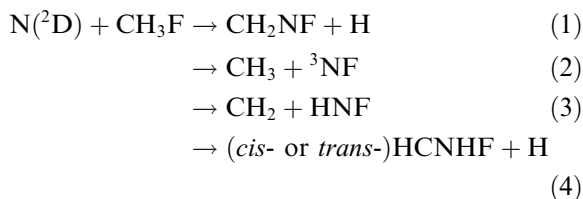
The extensive potential energy surface for the reaction of $N(^2D)$ and CH_3F has been studied using the G2MP2 level of theory. The calculations reveal that the reaction will lead to the intermediate *trans*- CH_3NF firstly, which subsequently decomposes and isomerizes to products. Based on the present ab initio potential energy surface, the production channel, $CH_2NF + H$ is the most feasible. The minimum-energy path is analyzed by an intrinsic reaction coordinate calculation. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

An electronically excited metastable nitrogen atom, $N(^2D)$, is known to be one of the important reactive species in the various fields such as atmospheric chemistry and combustion chemistry. However, its reactivity with CH_3X ($X = H, F$) is still unclear. The overall rate constants for the reaction of $N(^2D)$ with some hydrocarbon molecules have been measured [1,2]. Recently, Umemoto et al. [3] reported the nascent rotational and vibrational distributions of $NH(X^3\Sigma)$ produced in the reaction of $N(^2D)$ with CH_4 using a laser-induced fluorescence technique. They suggested that $N(^2D)$ inserts into the C–H bond. It is the first report in which the initial reaction product has

been detected. Takayanagi et al. [4] calculated the reaction $N(^2D)$ and CH_4 using a high-quality ab initio MO method and obtained information on possible reaction products. The reaction pathways to product $CH_2NH + H$ and $CH_3 + NH$ were found to be important. As far as we know, there are no theoretical reports about the reaction of $N(^2D)$ and CH_3F . Therefore, it is worth to be investigated as fundamental theoretical study, in order to compare with the reaction of $N(^2D)$ and CH_4 .

For the reaction of $N(^2D)$ with CH_3F , the probable pathways are suspected as follows:



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In this Letter, the reaction of $N(^2D)$ and CH_3F are studied by ab initio molecular orbital calculations. An extensive potential energy surface (PES) for the reaction is calculated by using high-level G2MP2 theory. Several possible production channels involved in the reaction are examined.

2. Computation methods

Ab initio calculations were carried out using the GAUSSIAN 98 program [5]. A reliable G2MP2 theory [6] was used to explore the lowest doublet reaction potential energy surface for the reaction of $N(^2D)$ and CH_3F . The geometries of reactants, products, intermediate (denoted as IM) and transition states (denoted as TS) were optimized at the MP2(full)/6-31G(d,p) level. The vibrational frequencies were obtained at the same level, in order to determine the nature of different stationary points and the zero-point-energy (ZPE) corrections (scaled by a factor of 0.95). A calculation that followed the minimum-energy path (MEP) down from the transition state in both directions (known as the IRC option in GAUSSIAN program) was also performed at the MP2(full)/6-31G(d,p) level. It confirmed that the transition state linked the desired reactants and products. Then, a series of high-level single energy calculations were carried out with the optimized geometries, and the barrier heights and reaction heats were obtained at the G2MP2 level.

Since some regions of the aforementioned PES were energetically close to a quartet potential energy surface ($N(^4S) + CH_3F$), spin contamination probably arose and led to severe errors in relative energies. In order to confirm our conclusion, it must be sure that the spin contamination is small enough. Indeed, the calculated $\langle S^2 \rangle$ values of the UHF wave functions along the potential curves were about 0.80 in the present calculation, indicating there existed moderately large spin contamination in our MP2(full) calculations. Thus, projected UMP2 [7–9] or single reference MP2 calculations using a ROHF wave function [10,11] were expected to provide more accurate results. Therefore, we used the projected MP2(full) energies instead of the default UMP2(full) energies in standard G2MP2 method. In the same while, the

ROMP2 calculations were carried out in order to compare with the projected UMP2 energies. The differences were small enough to neglect. According to that the eigenvalues after annihilation of the $\langle S^2 \rangle$ operator were very close to the theoretical predicted value 0.75 in general, the present calculations were reliable and the conclusions were satisfying.

3. Results and discussion

The optimized geometries of various stationary points (minima and saddle points) on the extensive potential energy surface for the $N(^2D) + CH_3F$ reaction are shown in Figs. 1 and 2. The harmonic vibrational frequencies for these stationary points are summarized in Table 1. The agreement between the calculated frequencies (scaled by 0.95) and available experimental data [12–15] is generally seem to be good, although the calculated values are somewhat larger than the experimental ones. Table 2 shows the total energies at the G2MP2 level calculated with the MP2(full)/6-31G(d,p) optimized geometries. The corresponding relative energies are also listed in Table 2. The overall energetic profile based on the G2MP2 energies for the reaction $N(^2D) + CH_3F$ is shown in Fig. 3. The theoretical studies show that many rearrangements with high barriers have to be involved.

3.1. The insertional reaction to form the intermediate (*trans-CH₃NF*)

The reaction between $N(^2D)$ and CH_3F takes place as they are approaching each other to interact on the doublet potential energy surface. As indicated in Table 2, the product, *trans-CH₃NF* (IM1) is 90.32 kcal/mol more stable than the reactant $N(^2D) + CH_3F$, at the G2MP2 level. The IM1 has C_s symmetry, in which the C–N bond is 1.444 Å and N–F bond is 1.392 Å at the MP2/6-31G(d,p) level. The structure of the CH_3 moiety is almost the same as that of stable CH_3F . Thus, the IM1 has higher internal energy, so that it can further decompose or isomerize to various products. There are four production channels in the present calculation, which will be discussed, respectively, in Sections 3.2 and 3.3.

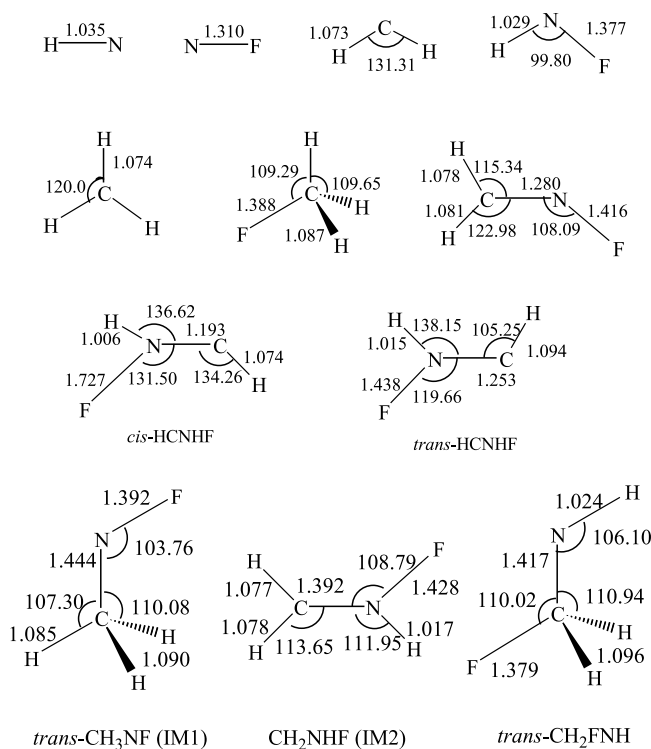


Fig. 1. The optimized geometries of various stationary points (minima) at the MP2(full)/6-31G(d, p) level. Bond lengths are in (Å), and bond angles are in (°).

As shown in Fig. 3, the intermediate, *trans*-CH₃NF (IM1) can be formed via a three-member ring barrier TS1. The barrier height is 29.54 kcal/mol relative to the reactants, N(²D) + CH₃F at the G2MP2 level. The transition state has C_s symmetry with an imaginary frequency 953 cm⁻¹. The breaking C–F bond is elongated by about 0.33 Å, while the C–H bonds are changed very slightly. The forming C–N bond is 1.925 Å and N–F bond is 1.555 Å, which are longer than those of the product IM1 about 0.48 and 0.16 Å, respectively. Thus, the transition state TS1 is a loose transition state. It will be discussed in detail in the following section.

3.2. Decomposition channels of IM1 (*trans*-CH₃NF)

As mentioned above, the intermediate IM1 is a highly activated complex. It is found that there are two decomposition channels as the following.

The energetically most favorable path is IM1 → CH₂NF + H, via a barrier TS2 of 40.78 kcal/mol height at the G2MP2 level. The C–H bond cleavage barrier TS2 has C₁ symmetry. The breaking C–H bond is elongated from 1.085 Å in IM1 to 1.833 Å. The other two C–H bonds are shortened slightly. The C–N bond is shortened by about 0.17 Å and the N–F bond is elongated by about 0.02 Å, which are close to those of the equilibrium value of product CH₂NF, 1.280 Å and 1.416 Å. Contrasted with the structure of the intermediate, there are severe changes of the bond angles. The N–F and C–H bonds turn around the C–N bond, so that these five atoms (besides the decomposing H atom) almost lie in the same plane as shown in Fig. 2. It is obvious that the TS2 is a product-like state. The total reaction pathway, N(²D) + CH₃F → CH₂NF + H, is exothermic by 55.42 kcal/mol at the G2MP2 level.

The other is a simple C–N bond scission channel of IM1 to form CH₃ + ³NF. This pathway is

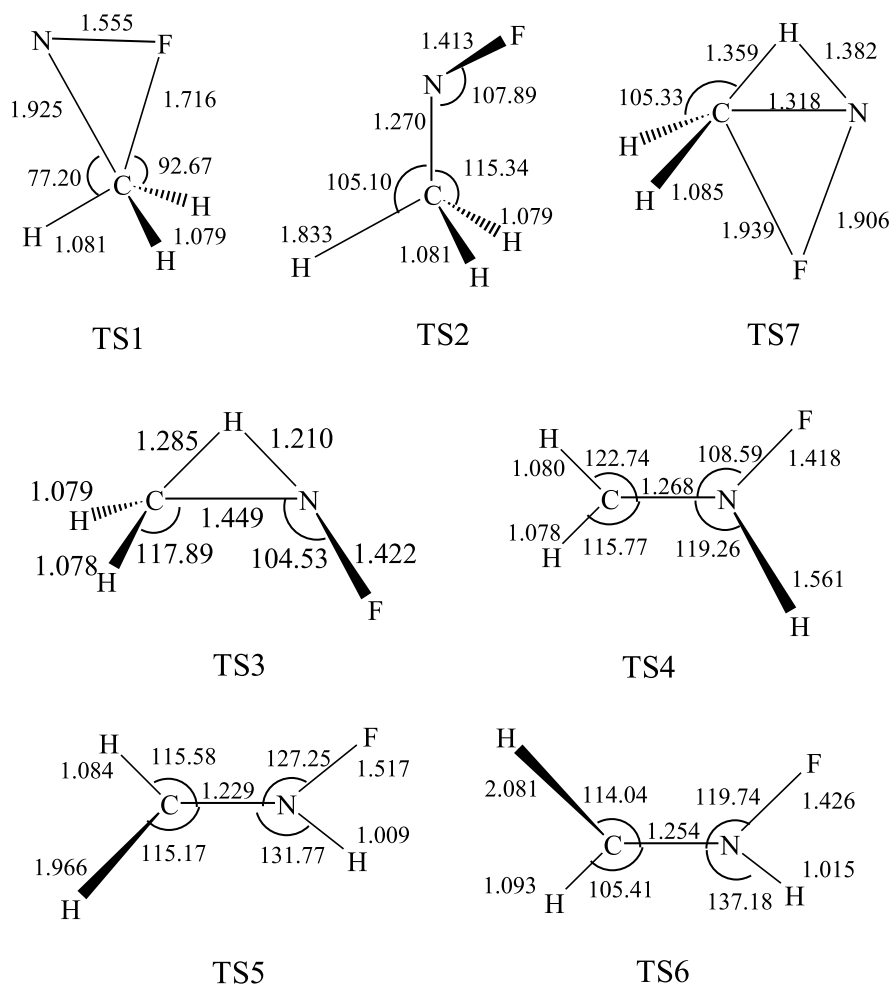


Fig. 2. The optimized geometries of various stationary points (saddle points) at the MP2(full)/6-31G(d,p) level. Bond lengths are in (Å), and bond angles are in (°).

endothermic by 66.05 kcal/mol, while the total pathway $\text{N}(^2\text{D}) + \text{CH}_3\text{F} \rightarrow \text{CH}_3 + ^3\text{NF}$ is exothermic by 24.27 kcal/mol.

3.3. Isomerization channels of IM1 (*trans*- CH_3NF)

In our ab initio MO calculation, two isomerization pathways are examined. The energetically favorable channel is the isomerization of IM1 to CH_2NHF (IM2), via a three-member ring barrier TS3 with 48.64 kcal/mol height. The transition state has C_1 symmetry with an imaginary frequency 2224 cm^{-1} . It suggests that it is a tight transition

state and probably exist the severe tunneling effect. At the MP2(full)/6-31G(d,p) level, the breaking C–H bond is elongated by about 0.20 Å and the forming N–H bond is 1.210 Å. The other C–H bonds are changed very slightly, which is also close to those of product IM2. The N–F bond is elongated by about 0.03 Å, close to that of IM2, 1.428 Å. Although this channel is endothermic by 12.80 kcal/mol, the product IM2 is still highly activated intermediate, 77.52 kcal/mol stable relative to initial reactants $\text{N}(^2\text{D}) + \text{CH}_3\text{F}$. Therefore, further decompositions will occur. Four production channels are studied as the following.

Table 1

Scaled MP2(full)/6-31G(d, p) harmonic vibrational frequencies of the reactants, products, intermediate and transition states in the reaction of $N(^2D) + CH_3F$

Species	Frequencies (cm^{-1}) ^a
CH ₃ F	1059 (1048) ^b , 1169 (1196), 1169 (1196), 1480 (1475), 1488 (1471), 1488 (1471), 2978 (2965), 3079 (2982), 3079 (2982)
CH ₃ NF (IM1)	200, 464, 918, 971, 1043, 1149, 1392, 1452, 1456, 2965, 3053, 3098
CH ₂ NHF (IM2)	303, 430, 717, 845, 910, 1112, 1214, 1383, 1450, 3101, 3228, 3394
<i>trans</i> - CH ₂ FNH	458, 498, 897, 964, 1088, 1183, 1217, 1407, 1454, 2917, 2965, 3344
CH ₂ NF	513, 774, 871, 948, 1128, 1365, 1605, 3079, 3204
<i>cis</i> - HCNHF	288, 568, 659, 776, 940, 972, 1995, 3233, 3566
<i>trans</i> - HCNHF	552, 640, 648, 977, 1071, 1352, 1507, 3001, 3405
CH ₃	375 (606), 1416 (1396), 1416 (1396), 3081 (3005), 3269 (3161), 3269 (3161)
CH ₂	1150 (1141), 3107, 3319 (3190)
HNF	1040 (1000), 1410 (1419), 3263
NF	1206 (1197)
TS1	953i ^c 536, 542, 779, 987, 1112, 1307, 1432, 1448, 3031, 3170, 3216
TS2	1232i, 325, 484, 525, 889, 921, 1082, 1142, 1356, 1578, 3077, 3203
TS3	2224i, 349, 454, 824, 871, 1057, 1103, 1263, 1380, 2431, 3084, 3221
TS4	1815i, 495, 514, 555, 772, 867, 988, 1131, 1364, 1594, 3089, 3216
TS5	929i, 202, 301, 439, 626, 921, 972, 1047, 1262, 1651, 3118, 3525
TS6	732i, 188, 253, 566, 649, 720, 1000, 1094, 1362, 1509, 3012, 3407
TS7	1710i, 236, 419, 544, 923, 1044, 1079, 1338, 1472, 1796, 3017, 3137

^a Scaled factor is 0.95.^b Values in parentheses indicate experimental data taken from [12–15].^c i represents imaginary frequency.

Table 2

Total energies (in hartree) and relative energies (in kcal/mol) of various species

Species	MP2/ 6-311G(d, p)	MP2/ 6-311+G(3df,2p)	QCISD/ 6-311G(d, p)	G2MP2	ΔE
$N(^2D) + CH_3F$	-193.78718	-193.90044	-193.85130	-193.97105	0.00
$N(^4S) + CH_3F$	-193.91368	-194.02033	-193.95733	-194.06585	-59.49
$CH_3 + ^3NF$	-193.84657	-193.95542	-193.89211	-194.00973	-24.27
$CH_2NF + H$	-193.88796	-194.00613	-193.92673	-194.05936	-55.42
<i>cis</i> -HCNHF + H	-193.83662	-193.96580	-193.87098	-194.01575	-28.05
<i>trans</i> -HCNHF + H	-193.81794	-193.93917	-193.85958	-193.99605	-15.69
$^3CH_2 + HNF$	-193.78656	-193.89743	-193.83142	-193.95258	11.59
<i>trans</i> -CH ₂ FNH	-193.99760	-194.11797	-194.03783	-194.16149	-119.50
CH ₃ NF[IM1]	-193.94972	-194.06699	-193.99390	-194.11499	-90.32
CH ₂ NHF[IM2]	-193.92944	-194.04974	-193.97030	-194.09459	-77.52
TS1	-193.74244	-193.86618	-193.79505	-193.92398	29.54
TS2	-193.88018	-193.99931	-193.91889	-194.04999	-49.54
TS3	-193.86925	-193.98958	-193.90849	-194.03747	-41.68
TS4	-193.87069	-193.98990	-193.91087	-194.04204	-44.55
TS5	-193.83139	-193.95400	-193.87237	-194.00813	-23.27
TS6	-193.81898	-193.94029	-193.86024	-193.99539	-15.27
TS7	-193.81444	-193.94400	-193.86355	-194.00412	-20.75

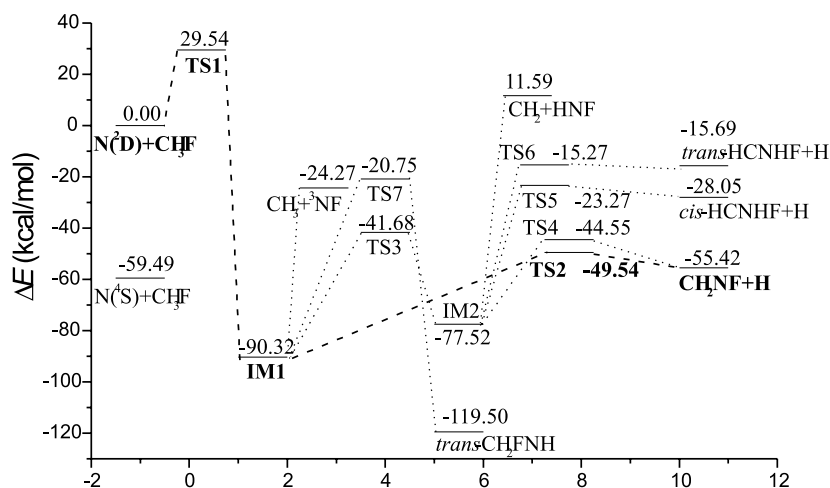


Fig. 3. The overall profile of the potential energy surface for the reaction $N(^2D) + CH_3F$, calculated at the G2MP2 level.

$CH_2NF + H$ can also be formed from dissociation process of the intermediate IM2, via a cleavage transition state TS4. The TS4 has C_1 symmetry with an imaginary frequency 1815 cm^{-1} . Any effects due to quantum mechanical tunneling should be much noticeable for this channel. The barrier height is 32.97 kcal/mol at the G2MP2 level. As shown in Fig. 2, the TS4 is a product-like state. The overall path, $IM2 \rightarrow CH_2NF + H$, is endothermic by 22.10 kcal/mol , while the total reaction pathway $N(^2D) + CH_3F \rightarrow CH_2NF + H$ is still exothermic as mentioned above.

As shown in Fig. 3, the IM2 can also decompose to *cis*- or *trans*-HCNHF + H via transition states TS5 or TS6, respectively. The barrier heights are 54.25 and 62.25 kcal/mol , respectively. The overall channels $IM2 \rightarrow (cis\text{- or }trans\text{-})HCNHF + H$ are endothermic by 49.47 and 61.83 kcal/mol .

There is one simple C–N bond scission process to form $^3CH_2 + HNF$ without any transition state. It is very endothermic by 89.11 kcal/mol , which is higher than the total energy of reactants $N(^2D) + CH_3F$ by 11.59 kcal/mol .

Another isomerization pathway is to product *trans*- CH_2FNH , via an abnormal four-member ring barrier TS7. This channel is exothermic by 29.18 kcal/mol at the G2MP2 level. However, the barrier height is 69.57 kcal/mol , which is too high due to the strong repulsion of the abnormal four-

member ring. It suggests that this channel is energetic unfavorable and very difficult to be performed. The breaking C–H and N–F bonds are elongated by 0.27 and 0.51 \AA , respectively. The forming N–H and C–F bonds are 1.382 and 1.939 \AA . It is abnormal that the C–N bond is shortened from 1.444 \AA in IM1 to 1.318 \AA , which is also shorter than that of *trans*- CH_2FNH (1.417 \AA). It is possibly due to that F atom is far away from the C–N bond.

3.4. Minimum-energy path for the insertional reaction

Although the saddle point (TS1) geometry for the $N(^2D) + CH_3F$ reaction was characterized, it is still unclear whether the reaction is insertional or not. Therefore, we have carried out IRC calculations to illustrate the reaction mechanism with the MP2(full)/6-31G(d, p) method. The MEP and the corresponding geometries are shown in Fig. 4.

In both of the negative and positive reaction coordinate region, the MEP refers to the local minimums, the initial reactants, $N(^2D) + CH_3F$, and the product *trans*- CH_3NF (IM1), respectively. Although the reaction coordinate region is not so large that the MEP could not approach the local minimums, it is confirmed that the transition state

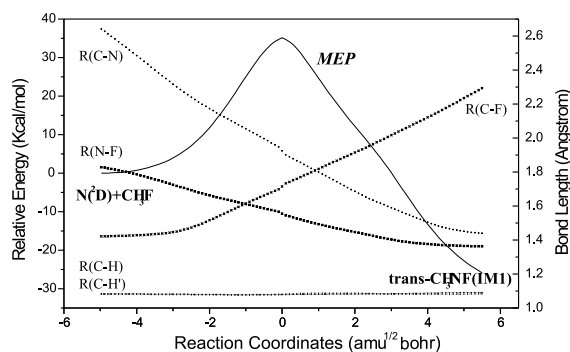


Fig. 4. Minimum-energy path (MEP) for the reaction $\text{N}(^2\text{D}) + \text{CH}_3\text{F} \xrightarrow{\text{TS1}} \text{trans-CH}_3\text{NF}$ (IM1). A total of 106 points along the reaction coordinate (s) are shown. The corresponding geometries (bond lengths) of these points are also shown by various symbols.

TS1 origins from the initial reactants and links the desired product.

From point ($s = -5.0$) to point ($s = 5.5$), the distance between N and C atoms is shortened rapidly to form the C–N bond. On the contrary, the C–F bond length is increased rapidly to break out. In the meanwhile, the distance between N and F atoms is shortened to form the N–F bond. The C–N and N–F bond lengths are 1.445 and 1.363 Å, respectively, which are close to the equilibrium values of IM1 (1.444 and 1.392 Å). The three C–H bonds are kept in this reaction process. Thus, the product *trans*-CH₃NF (IM1) would be formed.

3.5. Discussion on the present calculation

There should also exist H₂ or HF molecular elimination channels from the intermediate complexes. However, the barrier height for such processes may be expected to be very large. For instance, Walch [16] calculated the barrier heights for the $\text{CH}_3\text{OH} \rightarrow \text{HCOH} + \text{H}_2$ and $\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{CO} + \text{H}_2$ reactions using a high-quality ab initio MO method, which have been reported to be about 85 and 92 kcal/mol, respectively. Therefore, we neglect the H₂ and HF elimination channels in this Letter, although such channels would be important for larger excess energy.

Takayanagi et al. [4] confirmed that $\text{N}(^2\text{D})$ would insert into the C–H bond in CH₄ to form

the intermediate *trans*-CH₃NH, and the present results are similar to their conclusions. The present barrier height is 29.54 kcal/mol, which is larger than that of the reaction $\text{N}(^2\text{D}) + \text{CH}_4$, 5.5 kcal/mol. It seems to be reasonable, because the more excited energy will be needed to break out the stronger C–F bond energy. That is, F atom takes more effects on the barrier height for the insertion reaction than H atom, due to its strong electron affinity. The most feasible production pathways of $\text{N}(^2\text{D})$ with CH₄ and CH₃F reactions are very similar as $\text{H} + \text{CH}_2\text{NH}$ and $\text{H} + \text{CH}_2\text{NF}$.

Consequently, the conclusion derived from the energy diagram shown in Fig. 3 is that the most important production channel for the $\text{N}(^2\text{D}) + \text{CH}_3\text{F}$ reaction is $\text{CH}_2\text{NF} + \text{H}$.

4. Conclusion

Ab initio calculations have been carried out to study the possible production pathways in the $\text{N}(^2\text{D}) + \text{CH}_3\text{F}$ reaction. Among the probable processes considered, the reaction pathway to product $\text{CH}_2\text{NF} + \text{H}$ is most feasible. The IRC calculations have also been performed to understand the detailed mechanism of the $\text{N}(^2\text{D}) + \text{CH}_3\text{F}$ reaction. It has been confirmed that $\text{N}(^2\text{D})$ inserts into the C–F bond in CH₃F to form the intermediate *trans*-CH₃NF, which will further decomposes or isomerizes to various products. Further experimental studies would be necessary to confirm our theoretical results.

Acknowledgements

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