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Theoretical Study of the Potential Energy Surfaces of Nitrogen-Rich Ion $N_4H_2F^+$

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The relevant parts of the potential energy surfaces of nitrogen-rich ion involving the synthesis and dissociation reaction pathways of $N_4H_2F^+$ (isomer **2**) and the isomerization reactions of $N_4H_2F^+$ isomers were investigated. Eight isomers and five transition state structures were optimized by Hartree−Fork, hybrid density functional theory, and MP2 methods. The barriers of synthesis and dissociation reactions for isomer **2** were predicted to be 68.2, 69.3, and 53.8 kcal/mol and 11.8, 30.8, and 25.8 kcal/mol corrected by zero-point vibrational energy at the above-mentioned three levels, respectively. The experimental synthesis of isomer **2** is a challenge because of the high barrier and exothermicity. However, in condensed phase using catalysts, it is perhaps feasible. The exothermicity of isomer **2** for the first step of dissociation is 48.4 kcal/mol, and isomer **2** is 134.1 kcal/mol higher than that of $N_2H^+ + HF + N_2$ at the MP2 level. The high oxidative property of the F atom, contained in the ion $N_4H_2F^+$, marks this cation as a high effectiveness high energy density material when combined with an appropriate energetic anion. In addition, the results involving the structures and stability of $N_4H_2F^+$ isomers were also reported.

Introduction

Nitrogen clusters, as high energy density materials (HEDMs), have been objects of several theoretical studies. Besides theoretical interest in the pure nitrogen cluster,[1−13] nitrogen-rich compounds have attracted interest as well on account of their possible use as HEDMs.[14−19] Bartlett[14] suggested some nitrogen-rich clusters formed by N, O, and H as HEDMs. Hammerl and Klapötke studied nitrogen-rich clusters CN_x in both experiment and theory.[15] Recently, Gagliardi and Pyykkö[16,17] studied the structures of ScN_7, N_5−metal−N_7, and their dissociation reaction pathways. We also designed some possible reaction pathways for synthesizing the nitrogen-rich ionic compounds N_8H^+ [18] and $N_7H_2^+$.[19] The problem for the researchers is to create polynitrogen or nitrogen-rich compounds that store energy and yet are stable enough for practical applications as HEDMs.

Stability and synthesis methods of nitrogen compounds are challenging questions due to their metastable nature. Gagliardi et al.[7,8] investigated the potential energy surfaces (PES) of even-numbered nitrogen clusters and discussed their dissociation barriers. Since the early works of Christe and co-workers[6] who synthesized the AsF_6^- salt of N_5^+ by reaction of $N_2F^+AsF_6^-$ with HN_3 in anhydrous hydrogen fluoride, some studies on the PES of nitrogen clusters have been reported in our previous works.[10,11,13,18] Recently, we have also designed a possible reaction pathway for synthesizing the nitrogen-rich ionic compound $N_4H_2F^+$ by reaction of N_2F^+ with *trans*-N_2H_2. The results involving the structures and stability of $N_4H_2F^+$ isomers are also reported in this paper.

The existence of N_2H_2 (diazene) was suggested as early as 1892 as an intermediate in the decomposition of azoformic acid.[20] The trans isomer was finally discovered in 1958 by mass spectrometry as a gaseous discharge product of hydrazine.[21] The compound plays a very important role in organic and inorganic chemistry fields.[22−24] Some reactions involving N_2H_2 were investigated on theory as well.[25,26] N_2F^+ can be obtained from $N_2F^+AsF_6^-$, and the salt $N_2F^+AsF_6^-$ was prepared from *cis*-N_2F_2 and AsF_5.[27−29]

Nitrogen-rich cation $N_4H_2F^+$ has never been reported. The cation combined with an appropriate anion can be used as a HEDM, for it contains not only the high energy density fragment N_4[5,12,30−35] but also the high oxidative property of the F atom. $N_4H_2F^+$ will release more energy and be a more effective HEDM when it dissociates because the molecule HF is smaller than N_2. Therefore, it is significant to find the synthesis pathway of pure nitrogen clusters and nitrogen-rich compounds. Theoretical data will provide useful information for experimental synthesis.

Computational Method

The geometries of the $N_4H_2F^+$ isomers and transition structures involved have been optimized by ab initio and density functional theory (DFT) methods at the levels of HF/6-31G**, B3LYP/6-31G**, and MP2/6-31G**, where B3LYP is a hybrid density functional method using Becke's three parameter nonlocal exchange functional[36] with the nonlocal correlation of Lee, Yang, and Parr,[37] and MP2 stands for the second-order Mϕller−Plesset (many-body) perturbation theory.[38] The designation 6-31G** refers to a standard split-valence double-ζ polarization basis set.[38] All calculations were carried out with the Gaussian 98 program package.[39] To characterize the nature of the stationary points and determine the zero-point vibrational energy (ZPVE) corrections, harmonic vibrational frequencies were also calculated at the levels of theory mentioned above. Stationary points were identified as either local minima (number of imaginary frequencies (NIMAG = 0)) or transition states (NIMAG = 1). To confirm that the given transition states

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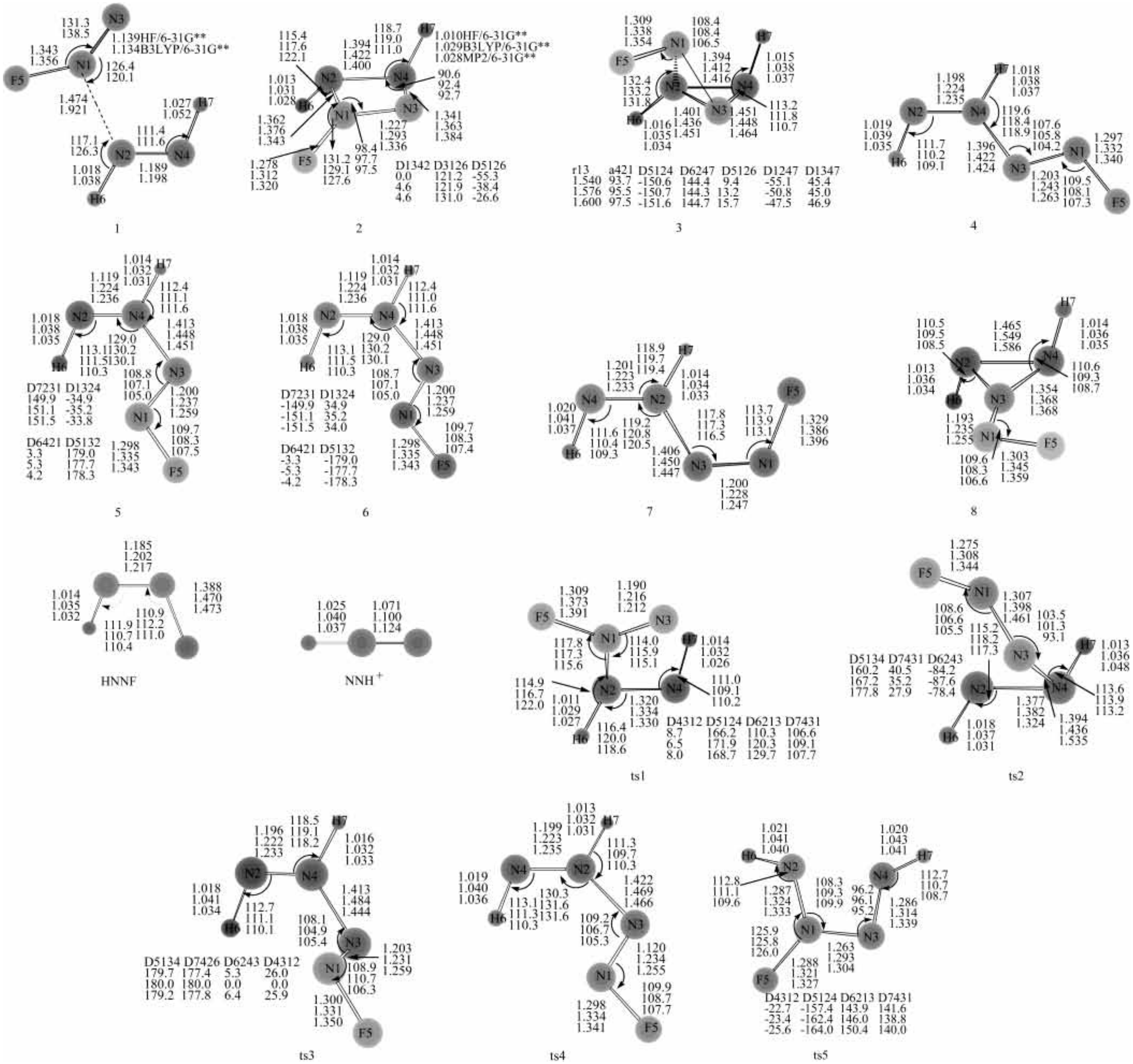

Figure 1. Geometries of structures involved on the $N_4H_2F^+$ PES.

connect reactants and products, minimum energy path calculations[40−44] were performed at the above levels with a coordinate stepsize of 0.1 (amu)$^{1/2}$ bohr.

The electron densities of species involved on the PES were calculated and analyzed using RHOCALC 2000.[45] RHOCALC 2000 takes the output (population file) from the Gaussian 98 program for our calculation and calculates the electron density data for a uniform three-dimensional grid. This program is used to analyze details of the electron density information for the whole molecule or for a fragment of the molecule using the additive fuzzing density fragmentation (AFDF) principle.[46−51] The molecular isodensity contour surfaces used for the visual inspection are calculated and visualized using the MOLCADII module[52−54] of the SYBYL molecular modeling package.[55]

Results and Discussion

1. Geometric Structures of the Species on the PES of $N_4H_2F^+$. Two reactants, eight isomers, and five transition structures were optimized at the HF/6-31G**, B3LYP/6-31G**, and MP2/6-31G** levels, and the geometric structures and parameters are given in Figure 1, while Tables 1 and 2 show their total energies and relative energies.

The isomer **1** is an ion−molecule complex on the potential energy curve of $N_4H_2F^+$ only at the HF/6-31G** and B3LYP/6-31G** levels, with C_s symmetry (see Figure 1). The ts**1** and ts**5** are transition state structures in the processes of synthesis and dissociation reactions for isomer **2**. These species, from isomers **3** to **8**, are six isomers $N_4H_2F^+$. The ts**2**, ts**3**, and ts**4** are transition state structures of the isomerization reaction among isomers **3**−**6**. Isomers **7** and **8** are two other isomers of $N_4H_2F^+$, with C_s and C_1 symmetry, respectively. Because of the property of the nitrogen−nitrogen bond, the energies of isomers containing more single bonds are high. Hence, the relative energies of isomers **2**, **3**, and **8** are higher than others. Isomer **4** is the most stable structure among all isomers with the lowest energy.

2. PES of the Synthesis Reaction. For this reaction, $N_2F^+ + trans\text{-}N_2H_2 \rightarrow N_4H_2F^+$, according to the results of intrinsic reaction coordinate (IRC), the possible mechanism at HF and

TABLE 1: Total Energies (Hartrees) and ZPVE (kcal/mol) of Species Involved on the PES of $N_4H_2F^+$

	ZPVE		
species	HF	B3LYP	MP2
N_2F^+ ($C_{\infty v}$)	−207.83103	−208.82114	−208.32434
	7.2	6.4	5.6
trans-H_2N_2 (C_{2h})	−109.99477	−110.63742	−110.33368
	19.7	17.8	18.0
N_2F^++ *trans*-H_2N_2	−317.82580	−319.45856	−318.65802
	26.9	24.2	23.6
isomer **1** (C_s)	−317.86025	−319.53153	*a*
	29.2	25.2	
ts**1** (C_1)	−317.75143	−319.42511	−318.57626
	29.1	25.7	26.1
isomer **2** (C_1)	−317.83984	−319.50678	−318.68220
	30.9	27.7	27.7
ts**5** (C_1)	−317.78064	−319.46201	−318.63847
	29.1	26.0	26.1
N_2H^+ + HN_2F	−317.94180	−319.56771	−318.76634
	25.4	22.8	32.2
N_2H^+ + HF + N_2	−318.09260	−319.67335	−318.90296
	21.6	19.6	19.0
isomer **3** (C_1)	−317.76583	−319.43498	−318.61637
	29.5	25.8	25.8
ts**2** (C_1)	−317.75755	−319.43039	−318.58811
	25.2	28.6	24.6
isomer **4** (C_s)	−317.91226	−319.55764	−318.73024
	30.3	27.0	27.1
ts**3** (C_1)	−317.90166	−319.55007	−318.72130
	29.9	26.7	26.8
isomer **5** (C_1)	−317.90378	−319.55090	−318.72461
	30.2	26.9	27.1
ts4 (C_s)	−317.90338	−319.55050	−318.72417
	30.1	26.8	26.9
isomer **6** (C_1)	−317.90378	−319.55090	−318.72461
	30.2	26.9	27.1
isomer **7** (C_s)	−317.90411	−319.55273	−318.72647
	30.1	26.5	26.8
isomer **8** (C_1)	−317.80815	−319.47299	−318.64563
	30.1	26.5	26.4

[a] At the MP2 level, the IRC result of ts1 shows ts1 connecting isomer 2 and N_2F^+ + *trans*-H_2N_2 directly.

TABLE 2: Relative Energies (kcal/mol) of Species Corrected by ZPVE Involved on the PES of $N_4H_2F^+$ with the Basis Set 6-31G**

species	HF	B3LY	MP2
N_2F^++ *trans*-H_2N_2	0.0	0.0	0.0
isomer **1** (C_s)	−19.3	−46.8	*a*
ts**1** (C_1)	48.9	22.5	53.8
isomer **2** (C_1)	−4.8	−26.8	−11.0
ts**5** (C_1)	7.0	4.0	14.8
N_2H^+ + HN_2F	−74.3	−69.9	−59.4
N_2H^+ + HF + N_2	−172.7	−139.4	−145.1
isomer **3** (C_1)	40.2	16.4	28.3
ts**2** (C_1)	48.8	22.1	44.9
isomer **4** (C_s)	−51.1	−59.4	−43.2
ts**3** (C_1)	−45.1	−54.9	−36.5
isomer **5** (C_1)	−45.7	−55.2	−38.3
ts**4** (C_s)	−45.5	−55.1	−38.2
isomer **6** (C_1)	−45.7	−55.2	−38.3
isomer **7** (C_s)	−45.9	−56.8	−39.8
isomer **8** (C_1)	14.4	6.8	10.6

[a] At the MP2 level, the IRC result of ts**1** shows ts**1** connecting isomer **2** and N_2F^+ + *trans*-H_2N_2.

B3LYP levels of theory is little different from that of MP2. The mechanism could be described as follows.

First, an ion−molecule complex was formed via the Coulomb force with no activation energy barrier by reactants N_2F^+ and *trans*-N_2H_2 at the HF/6-31G** and B3LYP/6-31G** levels. According to the charge distributions, the positive charge mostly distributes on the N1 atom of N_2F^+, while the negative charge mainly concentrates on atoms N2 and N4 of *trans*-N_2H_2. When the two species collide with each other, the atom N1 of N_2F^+ mainly attacks the atom N2 of *trans*-N_2H_2 via long-range Coulomb-induced force. Therefore, the complex can be formed with no activation energy barrier. The complex (isomer **1**), with C_s symmetry, is a local minimum on the PES for it has only real harmonic vibrational frequencies at the above-mentioned two levels. Following the isomer **1**, a transition structure (ts**1**) was found, in which the distances between the atoms N1 and N2, N3 and N4 were reduced to form new bonds, respectively. This transition structure was verified as being a saddle point of index 1 on the PES for it has precisely one imaginary vibrational frequency with C_1 symmetry. The reaction energy barrier height from isomer **1** to ts**1** corrected by ZPVE was predicted to be 69.3 kcal/mol at the B3LYP/6-31G** level. However, at the MP2 level, the result of IRC presented showed that the two reactants react directly via ts**1** to product (isomer **2**); that is, ts**1** connects reactants (N_2F^+ + *trans*-N_2H_2) and isomer **2** on the PES because the species obtained from the reverse direction of IRC separates into two parts (N_2F^+ + N_2H_2) when the bond N1−N2 is lengthened over 3.5 Å during the IRC calculation process. The high barrier height of 53.8 kcal/mol at the MP2/6-31G** level is in agreement on those of the other two methods. Although the experimental synthesis of this compound under normal conditions is not likely due to the higher barrier, in the condensed phase using catalyst, it might be possible.

Along the PES of $N_4H_2F^+$, when the bonds N1−N2 and N3−N4 are fully formed, the product $N_4H_2F^+$ (isomer **2**) was found, in which the bond distances between the atoms N1 and N2 and the atoms N3 and N4 were reduced to 1.343 and 1.384 Å at the MP2/6-31G** level, respectively.

To verify the reaction pathway, a calculation of IRC was performed starting from each corresponding transition structure at the levels of HF/6-31G**, B3LYP/6-31G**, and MP2/6-31G**, respectively. The geometries of the forward and reverse directions obtained from the IRC calculations are very close to isomer **1** and isomer **2** at the first two levels and are close to N_2F^+ + *trans*-N_2H_2 and isomer **2** at the MP2 level.

The reaction only occurs between N_2F^+ and *trans*-N_2H_2; that is, N_2F^+ reacts with N_2H_2 selectively (it only reacts with *trans*-N_2H_2 and does not react with *cis*-N_2H_2). The relative energy of the product (isomer **2**) is lower than that of the reactants; therefore, the outlined synthesis of $N_4H_2F^+$ by *trans*-N_2H_2 and N_2F^+ is an exothermic reaction. The calculations predict the exothermicity of $N_2F^+ + trans\text{-}N_2H_2 \rightarrow N_4H_2F^+$ as being 4.8, 26.8, and 11.0 kcal/mol at the above-mentioned three levels. Because of the high barrier and low exothermicity of the reaction, it is more likely to occur at high temperature or using catalysts but difficult under normal conditions.

3. Stability and High Energy Density Property of Isomer 2. Stability and high energy density property of isomer **2** were studied by the barrier and exothermicity of the dissociation reaction at the above-mentioned three levels. The dissociation barriers of isomer **2** were predicted to be 11.8, 30.8, and 25.8 kcal/mol, and the heat given off by the process of isomer **2** → HN_2F + N_2H^+ was 69.5, 43.1, and 48.4 kcal/mol at the HF/6-31G**, B3LYP/6-31G**, and MP2/6-31G** levels. The dissociation process of isomer **2** is that of N2−N4 and N1−N3 broken. If isomer **2** can further dissociate into N_2H^+ + N_2 + HF, energies of 167.9, 112.6, and 134.1 kcal/mol will be given off at the above-mentioned three levels. The moderate barrier of dissociation and the large energy given off imply that the isomer **2** is stable enough to be a good candidate as HEDM,

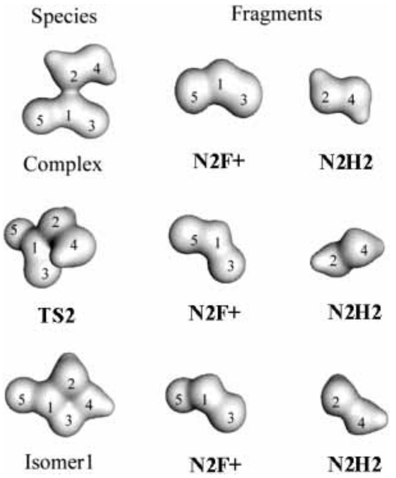

Figure 2. Approximate isodensity surfaces constructed using the RHOCLC2000 and MOLCAD II programs for the value 0.1 au of threshold density for the species and fragments on the relevant part of the synthesis reaction PES.

when combined with an appropriate anion such as nitrate, perchlorate, dinitramide, etc.

The salt of cation $N_4H_2F^+$ can be considered as a HEDM, not only because it contains a N_4 cluster but also because of the high oxidative property of the F atom and the smaller molecule HF. Therefore, in the forthcoming study, we shall investigate the mechanism of the dissociation reaction in order to understand the properties of the salt of $N_4H_2F^+$ as HEDM.

4. Isomerization Reactions. On the PES of $N_4H_2F^+$, the isomerization reactions involving four isomers among isomers **3**−**6** were studied. The isomerization reaction from isomer **3** to **4** is an exothermic process with 91.3, 75.8, and 71.5 kcal/mol at the above-mentioned three levels, respectively. The isomer **3** transferring into **4** is easy because of the low barrier of 8.6, 5.7, and 16.6 kcal/mol. The isomerization is the process of the fragment N1−F5 rotating around the center atom N3, N2−N3 lengthening, and N2−N4 shortening. The ts**3** is the transition state structure of isomerization from isomer **4** to **5**. The barrier heights of the reaction only are 6.0, 4.5, and 6.7 kcal/mol. This isomerization is only the fragment N1−F5 rotating around the center atom N3, and other parameters change slightly. The ts**4** is a transition state of the isomerization reaction from isomer **5** to **6**. The two isomers must exist together in one system because the barrier is so low (0.1−0.2 kcal/mol). This reaction is just a transition of the fragment N1−F5 up or down the plane of N3−N4−N2−H7; that is, isomers **5** and **6** are coupled mirror structures. The dissociation reactions of these isomers will be investigated in the forthcoming study.

5. Analysis of Electron Density of Species on the Synthesis Part PES of $N_4H_2F^+$. The fragment electron densities of N_2F^+, *trans*-N_2H_2, and isomer **2** were calculated at the reactant stage, the isomer **1** stage, the transition state (ts**1**) stage, and the product (isomer **2**) stage of the reaction utilizing the program RHOCALC[45] at the HF/6-31G** level.

As the reaction proceeds along the PES of the synthesis reaction, the changes of the electron density of the fragments N_2F^+ and H_2N_2 are visually apparent in Figure 2. The shape of electron density of N_2F^+ has visibly changed by the time the reactants are converted to the transition structure, whereas the isolated ion N_2F^+ (C_{2v}) is a linear structure. Additionally, the electron density has increased between atoms N1 and N2 at the transition state stage. Then, the bond N1−N2 has been formed and the distance between N3 and N4 has also been shortened. Whereas some of the results of the visual electron density analysis, which agree with that of the IRC calculation, offer evidence to display the process of $N_4H_2F^+$ forming, nevertheless, electron density visualization is a subjective process and can be error prone. Therefore, by utilizing the shape group method[39−44] and the corresponding numerical shape similarity measure, the confirmation of the visualization process was undertaken. Table 3 shows the shape similarity measures of the various electron density fragments relative to that of the isolated molecules as the fragments occur in the various steps of synthesis reaction.

TABLE 3: Shape Group Similarity Measures for the Electron Density Fragments of the Synthesis Process of Isomer 2

	N_2F^+	H_2N_2	$N_4H_2F^+$
starting molecules	1.0000	1.0000	
complex (isomer **1**)	0.5182	0.6249	0.5824
transition structure (ts**1**)	0.4780	0.5552	0.6598
product (isomer **2**)			1.0000

As the reaction proceeds to the isomer **1** stage, notable differences in the shape of the N_2F^+ ion occur. The differences in the shape of N_2F^+ ion are large because the electron density of N1 will tend to dominate that of the molecule. Thus, at the isomer **1** stage, a large electron density change has already occurred due to the Coulombic interaction of atoms N1 and N2. This change is also reflected in the shape change of N_2F^+ in the isomer **1** stage relative to the isolated ion. The shape similarity measure of the $N_4H_2F^+$ fragment in the isomer **1**, as compared with the product ion, is not high, which means that formal N1−N2 and N3−N4 bonds have most likely not yet been created completely at the stage.

As the reaction proceeds through ts**1** to the isomer **2** stage, the electron density of the molecules is further changed relative to the original molecules, indicating signs of bond formation. The similarity measure value of 0.6598 indicates that $N_4H_2F^+$ is becoming a more distinct entity in the transition state (ts**1**). By the time the isomer **2** stage is reached, the complete bond formation in the reaction occurs during the process from ts**1** to isomer **2**.

Summary

All calculations on the PES of synthesizing $N_4H_2F^+$ by *trans*-N_2H_2 and N_2F^+ showed that it is an exothermic reaction with a high barrier. The high barrier height of the synthesis pathway implies that the reaction cannot occur under normal conditions. The higher barrier of dissociation reaction and the large amount of energy given off imply that cation isomer **2** is stable enough to be a good candidate as HEDM, when combined with an appropriate anion such as nitrate, perchlorate, dinitramide, etc.

The reaction we studied is presumed to occur rarely in the gas phase, if most of the reactants are isolated. We estimate, however, that the barrier may be lower in the condensed phase. The high oxidative property of the F atom and possible dissociation products containing small molecules implies that the cation $N_4H_2F^+$ is likely a good candidate as a HEDM. It is possible that a condensed phase reaction would eventually be the optional choice. In such a case, the actual charges at various nitrogen atoms in the context of interactions between neighbor molecules will likely become important factors that computationally complicate the problem considerably. In a forthcoming study, we shall attempt to investigate these effects and do some further investigations of this reaction.

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