**Atmospheric chemical behaviours of C4F7N by DFT method: The relationship between electronic structure and atmosphere lifetime**

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**Abstract**

C4F7N with excellent insulation performance has been proposed to replace the traditional SF6 as a new insulating medium in power equipment. In the present study, the molecular structure and radiative efficiency (RE) of C4F7N are calculated and compared with SF6 based on DFT calculation. The decomposition of pure C4F7N and the basic interactions between C4F7N and hydroxyl radical in the constructed co-crystal of C4F7N-H2O have been simulated by applying Monte-Carlo calculation and Car-Parrinello molecular dynamics (CPMD) method, in order to obtain reasonable and full-scale atmospheric dissociation processes. Then the detailed decomposition pathways are learned with DFT method of M062X. The rate constants of different pathways are further applied for calculating the atmosphere lifetime of C4F7N, to evaluate the possibility of applying it as an alternative gas of SF6 in power equipment. All the atmospheric chemical behaviours are determined by electronic structure and reflected by the decomposition pathways of C4F7N with interacting with hydroxyl radicals. Rather than traditional hypothesizing reaction models, this study provides a reasonable and practicable method to evaluate more alternative protective gas for understand the greenhouse effect.

*Keywords*: C4F7N; Car-Parrinello molecular dynamics; Atmospheric dissociation; radiative efficiency; atmosphere lifetime

**1. Introduction**

Sulfur hexafluoride (SF6) is widely used in high-voltage insulation equipment because its excellent dielectric strength, heat transfer capacity and electric arcs interruption [1]. However, the atmospheric lifetime of SF6 is 3200 years with 100-year time horizon global warming potential (GWP100) of 23500[2]. Therefore, large scale usage of SF6 leads to more and more serious global warming risk[3-4]. Moreover, SF6 generates H2S, SO2, SOF2 and SO2F2 under high temperature, which further accelerates the insulation aging of insulation equipment [5-6]. So it’s necessary to develop alternative low-GWP insulating gas, such as CH3/CH3CH2I[7], CF3(CF2)n(CH2)2OH[8-9], CF3COOCH3[10] and (CF3)2CHOCF3/CF3OCF2CF2H[11]. But their applications are hindered by the polluted products, or extra high liquefaction temperature.

Until 2016, Minnesota Mining and Manufacturing (3 MTM) reported a new insulating gas, C4F7N (*i*-PFBN, heptafluoroisobutyronitrile), with 2.2 times the insulating properties of pure SF6. As an odorless colorless and non-flammable insulting gas, its ozone depletion index (ODP) is 0, with the atmospheric lifetime of 22 years and GWP of 2400[12-15]. Caused by such excellent properties, Pilot gas-insulated bus bars have been installed in a substation in England, and several 145 kV gas-insulated substations are planned in Europe [16]. However, due to the containing cyano group (-CN), the branched studies of CF3CN, CF3CF2CN and CF3CF2CF2CN [17] indicate that the possible toxic products of C2F5CN, CF3CN, COF2, CF4, C2N2 and C3F8 may threaten the environment and high-voltage insulating equipment [18]. The toxicity of C4F7N should be clarified based on a reasonable kinetic study. Moreover, atmospheric lifetime is an important indicator to evaluate the accompanied global warming risk of greenhouse gas, which is quite expensive to obtain it in the experiments [19-25]. Here we hope to apply CPMD method to provide more reasonable full dissociation pathways rather than the only hypothesized reaction models in tradition [22-23, 25], to obtain a reasonable atmospheric lifetime.

In the manuscript, we first compared the electronic structures and radiative efficiency (RE) of molecular SF6 and C4F7N based on the optimized structures. Because hydroxyl radical is the main component in atmosphere to interact with greenhouse gas, we construct the co-crystal structure of C4F7N and H2O with the molar ratio of 1:1 by Monte-Carlo method to simulate the full dissociation pathways of C4F7N with hydroxyl radicals in atmosphere by CPMD method. The decomposition of pure C4F7N is also calculated to obtain the products for understanding the toxicity. Then three pathways are summarized as the representative dissociation pathways of C4F7N in atmosphere based on the dynamic trajectories. The high accurate potential energy curves are obtained to continuously evaluating the atmosphere lifetime of C4F7N.

**2. Methods**

We first optimize molecular structures of C4F7N and SF6 under the level of M062X/def2tzvp [26] in Gaussian 09 package [27]. The electronic structures including the Wiberg bond index (WBI), atomic charges, electro statistic potentials and polarizability are calculated under the same level. To obtain the reasonable interaction pathways for the dissociation of C4F7N with hydroxyl radial in atmosphere, we pack the co-crystal by mixing C4F7N and H2O. The optimized gas-phase C4F7N and H2O are set as the motion groups, which are allowed to rotate or translate in the packing with all the relative atoms in molecule fixed. The corresponding crystal structures have been predicted by using Monte-Carlo (MC) method based on the Belsky’s theory [28]with the universal force field (UFF) [29] in Forcite and Polymorph [30] package. The periodic structure of pure C4F7N are also packed for comparing with C4F7N-H2O with the similar methods.

Then, the packed crystal structures of C4F7N and C4F7N-H2O are optimized by using the MS-CASTEP [31] program and the exchange-correlation function of GGA-PBE[32-33]. The ultrasoft pseudopotentials [34]with valence states N(2s22p3), O(2s22p4) and H(1s1) are used to describe the valence electrons. The cutoff energy of Plane wave functions has been set as 340 eV in the optimization. The k-point grid of 3×1×2 and 3×1×2 Monkhorst–Pack meshes [35]are used to describe the Brillouin-zones.

Based on the optimized crystal structures, we directly increase the temperature for the two structures to 2500 K for 5 ps to equilibrate the system after convergence of wave function and optimization with NVT ensemble in CPMD simulations. Then the temperature has been continuously increased to 3000 K for another 21 ps. The final temperature is converged at 3000 K. The total length of 26 ps (260000 steps) is enough for obtaining the interaction pathways.

Finally, the active energies in the typical three dissociation pathways are obtained based on the CPMD trajectories. Then atmosphere lifetime (τ) is obtained based on Equation (1) [36], where the rate constants are obtained based on traditional state theory (TST) as showed in Equation (2). Τ is the atmosphere lifetime for CO2 equals to 150 year [37].

τ = α/(kOH·COH ) (1)

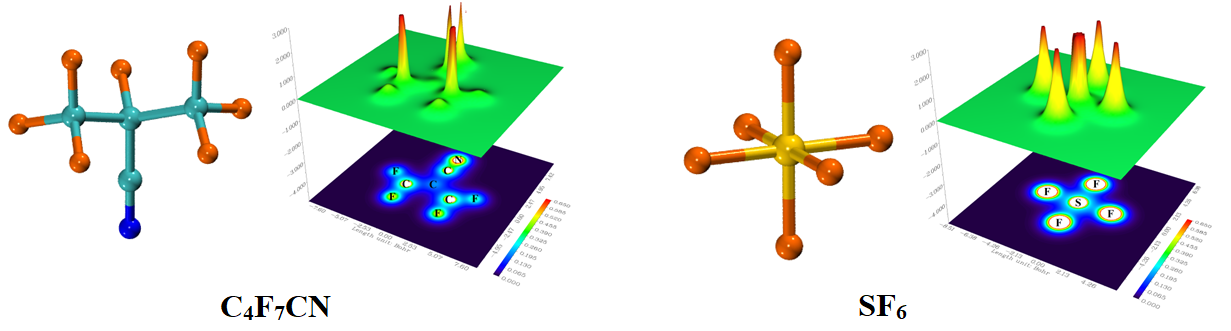
 (2)

In Equation (1), α is the experienced constant equaling to 2.1. *k*OH is the rate constant of reaction between the greenhouse gas and hydroxyl radical, which has been obtained by Equation (2). *C*OH is the concentration of hydroxyl in the atmosphere, which is 1×106 mol·cm-3 [36]. In Equation (2),  is energy barrier of the corresponding pathway.

**3. Results and Discussions**

**3.1 The gas phase structures**

The molecular structures of C4F7N and SF6 are optimized under the theoretical level of M062X/def2tzvp. The optimized structures with the corresponding charge distribution maps have been summarized in **Fig. 1**.



**Fig. 1**. The optimized structures of gas-phase C4F7N and SF6 with the corresponding charge distribution. Green: C; Orange: F; Blue: N; Yellow: S.

We have compared the structural properties in **Table 1**. SF6 as a traditional insulation gas, adopts D4h symmetry with the HOMO-LUMO gap of 7.76 eV. The calculated volume is 137.7 Å3. The bond length of S-F bond is 1.59 Å, which is slightly longer than the single S-F bond length of 1.55 Å, indicating the six S-F bonds are polarized. Actually, the bond polarization is reflected by the charge distribution, where the NBO atomic charges on S and F are 2.65 and -0.44 a.u. Based on the optimized molecule, the vertical ionization energy (VIE) and electronegativity are 286.7 kcal/mol and 3.88 eV. Therefore, with the extra high stability and excellent electron-withdraw ability, the S-F bonds (with the dipole moment of 1.12×10-29 C·m) are able to absorb electrons generated by ionization process between two electrodes.

C4F7N is smaller than that of SF6 with the molecular volume of 82.58 Å3. C≡N bond is the highest polarized bond with the bond length of 1.15 Å and dipole moment of 5.41×10-30 C·m, where the atomic charge is -0.210 and 0.209 a.u. Although the polarizability is lower than that of SF6, but the two π bonds in C≡N substitute improve the ability of absorbing electrons. Therefore, both VIE and electronegativity is larger than that of SF6, indicating C4F7N exhibits better performance in the process of arc extinction.

**Table 1.** The molecular volume, HOMO-LUMO gap, vertical ionization energy (VIE), electronegativity and Wiberg bond index of C4F7N and SF6 under the level of M062X/def2tzvp.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molecule | Molecular Volume (Å3) | HOMO-LUMO gap (eV) | VIE (kcal/mol) | Electronegativity (eV) |
| SF6 | 137.7 | 7.76 | 286.7 | 3.88 |
| WBI | S-F: 0.72 | | | |
| C4F7N | 82.58 | 8.10 | 336.5 | 4.05 |
| WBI | C-F: 0.93; C-C(F) 0.92; C-(CN): 0.98; C≡N: 2.96 | | | |

Furthermore, based on the Pinnock’s method [38] as Equation (3), we have predicted the radiative efficiency (RE) of C4F7N in **Table 2**. Wherein,  (km/mol) is the infrared intensity.  is the binned radiative forcing from 0 ppbv to 1 ppbv on the unit area based on Pinnock’s work [38], where  (cm-1) is the Raman wave number.

 (3)

The detailed infrared intensity, Raman wave number and  values are summarized based on the calculation under the level of M062X/def2tzvp. Compared with the radiative efficiency of SF6 [39], which is 0.57 W·(m2·ppbv)-1, C4F7N with RE of 0.18 W·(m2·ppbv)-1 exhibits much lower radiative efficiency and advanced atmosphere performance.

**Table 2.** Infrared intensity, Raman wave number and the binned radiative forcing

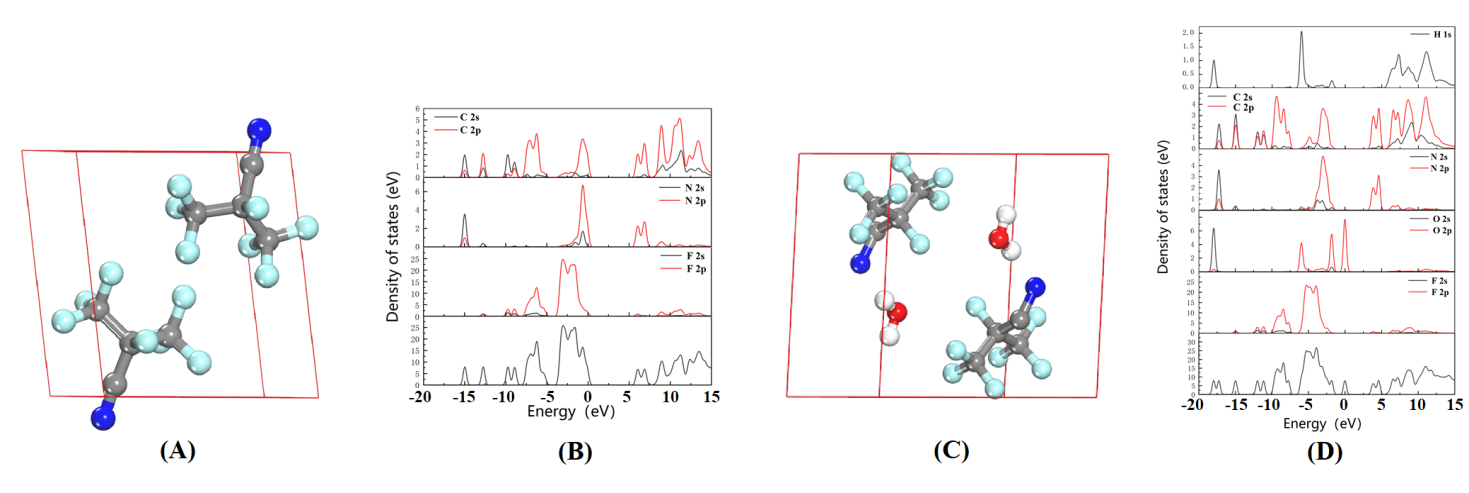
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | /cm-1 | /km·mol-1 | /10-3·W·m-2·(cm-1)-1·(10-18·cm2·mol-1)-1 | RE/ W·(m2·ppbv)-1 |
| C4F7N | 1320 | 390 | 0.333 | 0.18 |
| 790 | 20 | 2.94 |
| SF6 |  |  |  | 0.57 [39] |

**3.2 Crystal Structures of C4F7N and C4F7N-H2O**

As we discussed in the Method and the supplementary information, we apply Monte-Carlo method to predict a co-crystal structureof C4F7N-H2O as a mixed system for understanding the interactions of C4F7N and hydroxyl in the simulation of atmosphere dissociation. The optimized structures of C4F7N and C4F7N-H2O prepared for the motion groups in Polymorph code showed in **Fig S1** (supporting information). Actually, the predicted crystal structure provides us only a reasonable initial position for each atom. As a comparison, we predict the periodic structure of C4F7N with the same methods. The detailed information mentioned in **SI-Fig S2** and **SI-Table S1**. On the basis of the predicted structures (**SI-Fig S3**) with the lowest total energy by polymorph code, the optimized structures of C4F7N and C4F7N-H2O are completed in CASTEP with GGA-PBE method (**SI-Table S2**). The optimized structures with the corresponding the DOS maps are showed in **Fig. 2**. All the details of predictions are summarized in SI- section 1 and section 2.

The solidate C4F7N adopts *P*21 space group with the bandgap of 5.1 eV, where the cell parameters are *a* = 8.03 Å, *b* = 5.22 Å, *c* = 7.43 Å, α = 90.0°, β = 82.6°, γ = 90°. The highest energy band ranged at -5 eV~0 eV is dominated by C 2*p*, N2*s*/2*p* and F 2*p* states. The density of states (DOS) analysis of C4F7N means that the active positions are C-F and C≡N bonds.

With the introducing of H2O, the space group of C4F7N-H2O is *P*1 with the band gap of 3.67 eV. the cell parameters are *a* = 5.35 Å, *b* = 10.02 Å, *c* = 8.70 Å, α = 95.25°, β = 124.06°, γ = 100.61°. The band near the Fermi level (-5eV~0 eV) is not only dominated by C 2*p*, N2*s*/2*p* states, but also dominated by O 2*p* states and has a very small contribution from H 1*s* states. We notice that N2*s*/2*p* states and F 2*p* states are both 1.5 eV lower than that in pure C4F7N, indicating the doped hydroxyl groups (molecular water) decrease the stability of C4F7N caused by the high active O 2*p* electronic states.



**Fig. 2.** The predicted crystal C4F7N and C4F7N-H2O with the corresponding DOS maps.

**3.3 The thermal decomposition of C4F7N and C4F7N-H2O**

As the reaction between greenhouse gas and hydroxyl radicals is the main dissociation pathway of C4F7N. We first apply CPMD method to understand the dissociation of C4F7N in atmosphere. The forcefield tests for dynamic study are summarized in SI-section 3 (**SI-Fig S4** and **Table S3**). The rearrangements of dissociation components take place by the decomposition and combination reactions during the dynamics simulation. As for comparison, we first obtain the decomposition pathways of pure C4F7N in scheme 1. To accelerate the decomposition, we set the temperature to 3000 K to observe the trajectories of the decomposition. Here we do not observe the cleavage of the carbon chains. However, CN group and fluorine radicals depart from the molecule successively with the splitting of C-(CN) bonds or C-F bonds, where the sequence is consistent with the results of the bond strength (WBI) in **Table 1**, where the polarized bond splits at first. With the generated active radicals at extra high temperature, the products probably are cyanides or fluorides based on **Scheme 1**.



**Scheme 1.** The decomposition pathway of pure C4F7N at 3000 K.

Then we confirm the three dissociation mechanisms of C4F7N with interacting with hydroxyl radicals in atmosphere as showed in scheme 2 ~ 4. In all the three ways, the dissociation of C4F7N is triggered by the splitting of C-(CN) bond, which is consistent of the first step in scheme 1 caused by the weakest bond strength in the molecule. The active fragment of  is the initial of the continuous chain-growth in the interaction with hydroxyl radicals in our simulation.



**Scheme 2.** The first pathway of the interaction between C4F7N and hydroxyl radical at 3000 K.

**Dissociation triggered by hydroxyl**: As showed in **Scheme 2**, water decomposes to generate hydroxyl radicals, which is the high active radical to attack the weakest C-CN bond to generate HOCN or C3F7OH. So the decomposition of C4F7N is triggered by hydroxyl radical in pathway (1). Then the reaction is continued by the synergetic interaction between -H and  to generate F2 and HF as the products as summarized in **Scheme 2**.



**Scheme 3.** The second pathway of the interaction between C4F7N and hydroxyl radical at 3000 K.

**Dissociation triggered by oxygen radical**: For pathway (2) in **Scheme 3**, the active center is oxygen of hydroxyl radical, where the lone pairs of oxygen close to the electron-deficient center of . Here, we notice the cleavage of C-(CF) bond proceeds with the combination of C-OH2 bond. The synergetic interaction between oxygen and active fragment of  induces the continue dissociation with the products of F2, HF and NO as summarized in **Scheme 3**.

**Dissociation triggered by hydrogen radical**: In **Scheme 4**, the dissociation in Pathway (3) is triggered by the competition between H radical and the center C atom in the active fragment of to combine with –F to form HF. Then oxygen further connect with the center C atom to lead to the further decomposition with the generation of F2, HF and NO as summarized in **Scheme 4**.



**Scheme 4.** The third pathway of the interaction between C4F7N and hydroxyl radical at 3000 K.

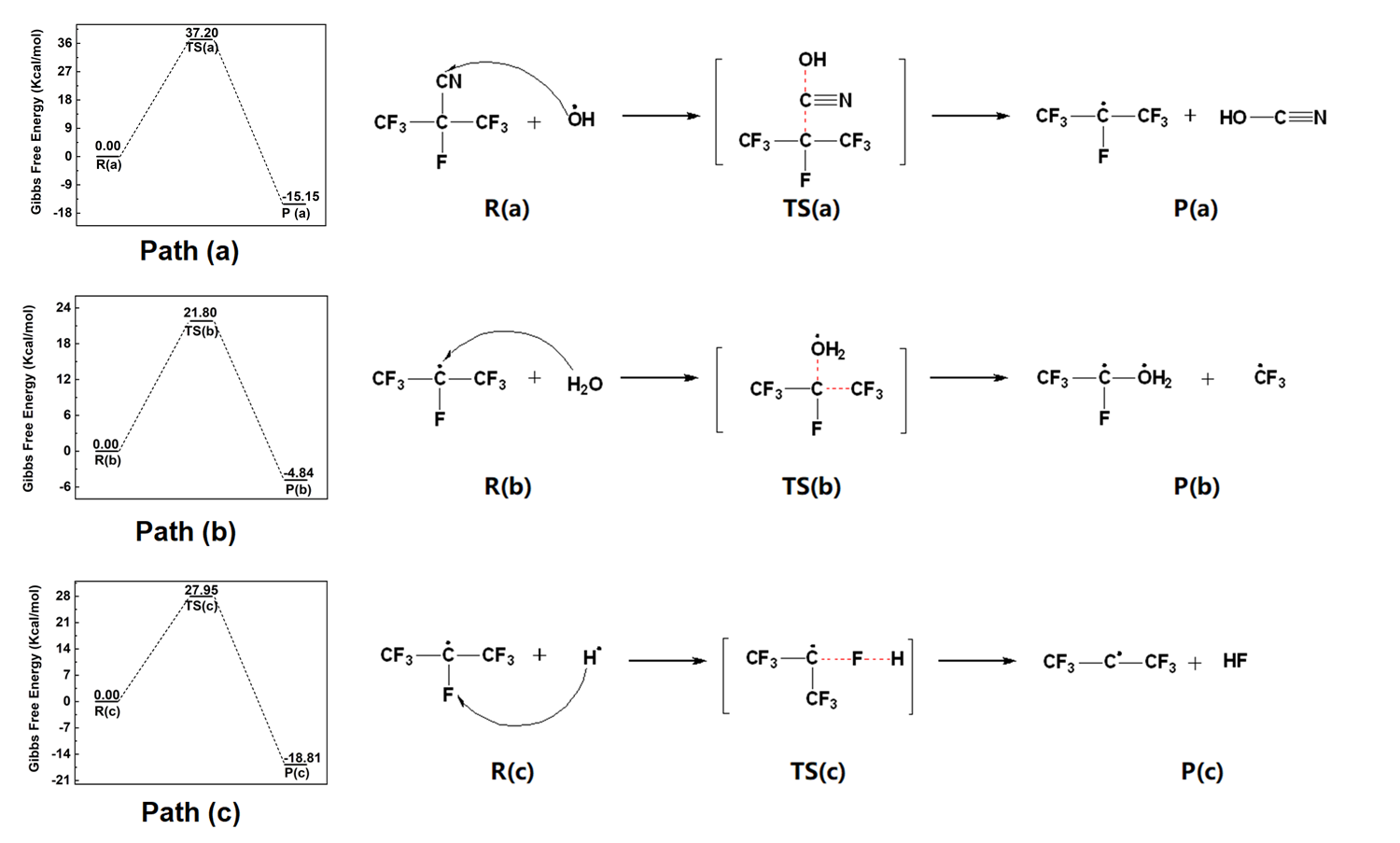
**3.4 Atmosphere lifetime**

In the atmosphere, the lifetime of greenhouse gas is dominated by the reaction rate in the interaction with hydroxyl radicals. Therefore, based on such three decomposition mechanisms in Scheme 2 ~scheme 4, we calculate three transition states in order to understand the reaction rates based on the transition state theory (TST). The three potential energy surfaces are summarized in **Fig. 3**. The energy barriers are summarized in **Table 3**. The three pathways represent the different trigger mechanisms based on CPMD trajectories. Obviously, the dissociation triggered by hydroxyl radicals showed in Path (b) is the preponderant pathways under the room temperature, where the activation energy is 21.8 kcal/mol, which is lower than that of Path (a) and Path (c). Based on TST, we calculate the rate constant of path (a)~(c) at 298 K.

Finally, the atmosphere lifetime of C4F7N can be obtained by Eq. (1). Although path (b) is the pathway with the lowest barrier, the lifetime is dominated by the rate-determined pathway (a), where the barrier is 37.20 kcal/mol, leading to the lifetime of 21.21 year. Compared with SF6, with the lifetime of 3400 year [39], C4F7N is the alterative replacement of SF6 as the protective gas in the in high-voltage insulation equipment.

**Table 3.** The energy barriers, rate constants and τ value of C4F7N

|  |  |  |  |
| --- | --- | --- | --- |
|  | Energy barrier (kcal· mol-1) | k  (mol-1· cm3· s-1) | τ  (year) |
| TS(a) | 37.20 | 3.14x10-15 | 21.21 |
| TS(b) | 21.80 | 6.26x10-4 | 1.06 x10-10 |
| TS(c) | 27.95 | 1.92 x10-8 | 3.46 x10-6 |



**Fig. 3.** The potential energy surfaces of pathway (a)~(c), with the corresponding chemical structures

**3.5 Conclusion**

In the present study, we apply DFT method to understand the relationship between the structure and the atmosphere chemical properties of C4F7N, in order to evaluate its possibility to be an alternative protective gas in the insulation equipment. The high polarized C≡N bond with π bonds is capable to effective absorb electrons generated by ionization process between two electrodes. Based on CPMD simulations, we obtain three dissociation pathways in the atmosphere of C4F7N, where the leaving group of CN generated the active C3F7 radical can be further activated by O radical, H radical and OH radical, where the preponderant pathway is the combination between C3F7 radical and O radical (from H2O). But the atmosphere lifetime is dominated the pathway with slowest rate, where the C3F7 decomposed triggered by OH radical shows the lifetime of 21.21 year. Considering the low RE value and extra short atmosphere lifetime of C4F7N, it is valuable to try to apply it as an alternative gas of SF6 in power equipment.

Moreover, compared with the traditional hypothesizing reaction models, this study provides more reasonable trajectories based on Ab initio molecular dynamic simulation to evaluate the atmosphere lifetime of C4F7N, which can be broaden to evaluate more alternative protective gas for understand the greenhouse effect.

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**References**

[1] A. J. Yang, D. W. Wang, X. H. Wang, J.-F. Chu, P. L. Lv, Y. Liu and M. Z. Rong, *IEEE ELECTR DEVICE L.* **2017**, *38(7)*, 963-966.

[2] L. Christophorou, J. Olthoff and D. Green, *NIST.* **1997**, *6,* 3-4.

[3] P. Agreement in *Report of The Conference of The Parties on Its Twenty-First Session, Held in Paris from 30 November to 13 December 2015*, **2015**.

[4] H. Wang, X. Lu, Y. Deng, Y. Sun, C. P. Nielsen, Y. Liu, G. Zhu, M. Bu, J. Bi and M. B. McElroy, *Nat. Sustain.* **2019**, *2(8)*, 748-754.

[5] H. Zhao, X. Li, K. Zhu, Q. Wang, H. Lin and X. Guo, *IEEE T DIELECT EL IN.* **2016**, *23(5)*, 2657-2667.

[6] S. Okabe, H. Goshima, A. Tanimura, S. Tsuru, Y. Yaegashi, E. Fujie and H. Okubo, *IEEE T DIELECT EL IN.* **2007**, *14(1)*, 83-90.

[7] J. Zhang, Y. Liang, S. Xie, J.-l. FENG, K. WANG and T.-l. ZHANG, *Chem Res Chin Univ.* **2012**, *28(6)*, 931-935.

[8] Y. Wang, J.Y. Liu, Z.-s. Li, L. Wang, J.-y. Wu and C.-c. Sun, *J. Phys. Chem. A.* **2006**, *110(17)*, 5853-5859.

[9] Y. Wang, J.-Y. Liu and Z.-S. Li, *Chem. Phys.* **2007**, *335(1)*, 28-36.

[10] B. K. Mishra and R. C. Deka, *J. Phys. Chem. A.* **2014**, *118(38)*, 8779-8786.

[11] M. P. Sulbaek Andersen, O. J. Nielsen, B. Karpichev, T. J. Wallington and S. P. Sander, *J. Phys. Chem. A.* **2012**, *116(24)*, 5806-5820.

[12] Y. Zhang, X. Zhang, C. Liu, Y. Li, Z. Cui and M. Fu, *Appl Spectrosc.* **2019**, *73(8)*, 917-926.

[13] Y. Li, X. Zhang, S. Xiao, Q. Chen, J. Tang, D. Chen and D. Wang, *Ind. Eng. Chem. Res.* **2018**, *57(14)*, 5173-5182.

[14] Y. Kieffel, F. Biquez, P. Ponchon and T. Irwin, *2015 IEEE Power Energy Soc general meeting* **2015**, 1-5.

[15] M. P. Sulbaek Andersen, M. Kyte, S. T. Andersen, C. J. Nielsen and O. J. Nielsen, *Environ.* **2017**, *51(3)*, 1321-1329.

[16] R. E. Plump and J. C. Devins in *Electrical apparatus and gaseous dielectric material therefor comprising perfluoroalkylnitrile*, **1962**.

[17] Y. Kieffel, T. Irwin, P. Ponchon and J. Owens, *IEEE POWER ENERGY M.* **2016**, *14(2)*, 32-39.

[18] C. Wang, X. Ai, Y. Zhang, Y. Tu, X. Yan and W. Liu, *IEEE T DIELECT EL IN.* **2019**, *26(6)*, 1949-1955.

[19] V. Oruç and A. G. Devecioğlu, *Int J Refrig.* **2021**, *128,* 242-251.

[20] G. Li, M. Eisele, H. Lee, Y. Hwang and R. Radermacher, *Energy Procedia.* **2014**, *68,* 819-831.

[21] L. Wang, C. Dang and E. Hihara, *Int J Refrig.* **2012**, *35(5)*, 1418-1429.

[22] G. A. Longo, C. Zilio, G. Righetti and J. S. Brown, *Exp. Therm. Fluid Sci.* **2014**, *57,* 293-300.

[23] M. Azzolin, A. Berto, S. Bortolin, L. Moro and D. Del Col, *Int J Refrig.* **2019**, *103,* 77-90.

[24] A. G. Devecioğlu and V. Oruc, *Energy Procedia.* **2015**, *75,* 1452-1457.

[25] P. Makhnatch and R. Khodabandeh, *Energy Procedia.* **2014**, *61(*2460-2463.

[26] Y. Zhao and D. G. Truhlar, *Theor Chem Acc.* **2008**, *120(1)*, 215-241.

[27] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson and H. Nakatsuji, Wallingford CT*.* **2016**, *421(*

[28] P. Zorkii, A. Razumaeva and V. Belsky, *Acta Crystallogr.* **1977**, *33(6)*, 1001-1004.

[29] A. K. Rappé, C. J. Casewit, K. Colwell, W. A. Goddard III and W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114(25)*, 10024-10035.

[30] W. A. Trzciński, S. Cudziło and L. Szymańczyk, *Propellants, Explosives, Pyrotechnics.* **2007**, *32(5)*, 392-400.

[31] M. Segall, P. J. Lindan, M. a. Probert, C. J. Pickard, P. J. Hasnip, S. Clark and M. Payne, *J. Phys. Condens. Matter.* **2002**, *14(11)*, 2717.

[32] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77(18)*, 3865.

[33] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J CHEM PHYS.* **2010**, *132(15)*, 154104.

[34] R. Car and M. Parrinello, *Phys. Rev. Lett.* **1985**, *55(22)*, 2471.

[35] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B.* **1976**, *13(12)*, 5188.

[36] Z. C. C. Q. L. L. Q. Rui, *Insulating Materials.* **2018**, *51(10)*, 78-82.

[37] F. Cherubini, G. Guest and A. H. Strømman, *Glob Change Biol Bioenergy.* **2012**, *4(6)*, 784-798.

[38] S. Pinnock, M. D. Hurley, K. P. Shine, T. J. Wallington and T. J. Smyth, *J GEOPHYS RES-ATMOS.* **1995**, *100(D11)*, 23227-23238.

[39] G. Myhre, D. Shindell, F. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J. Lamarque, D. Lee and B. Mendoza, *Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change.* **2013**, 659-740.