Study on Pyrolysis Characteristics of SF\textsubscript{6} in a Trace-Oxygen (O\textsubscript{2}) Environment: ReaxFF\textsubscript{SF\textsubscript{6}O} Force Field Optimization and Reactive Molecular Dynamics Simulation

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ABSTRACT: The ReaxFF\textsubscript{SF\textsubscript{6}O} force field for a SF\textsubscript{6}−O\textsubscript{2} system is developed based on the density functional theory (DFT) calculation data. Then, a series of molecular dynamics (MD) simulations were performed. The results show that the main oxygen-containing compounds that appeared in the MD simulation include SOF\textsubscript{4}, SOF\textsubscript{2}, and SO\textsubscript{2}F\textsubscript{2}. The relative quantitative relationship between SOF\textsubscript{2} and SOF\textsubscript{4} can be used to determine the fault temperature. Besides, under overheating conditions, O\textsubscript{2} rarely undergoes a self-cracking process to generate free O atoms. Instead, the basic route for O\textsubscript{2} to participate in the SF\textsubscript{6} pyrolysis process is X + Y + O\textsubscript{2} = XO + YO. Furthermore, the reactivity order of various groups to O\textsubscript{2} is (SF\textsubscript{2})\textsuperscript{*} > (SF\textsubscript{3})\textsuperscript{*} > (SF\textsubscript{4})\textsuperscript{*} > F\textsuperscript{*}, so O\textsubscript{2} is more likely to participate in the reaction by attacking (SF\textsubscript{3})\textsuperscript{*} or (SF\textsubscript{2})\textsuperscript{*} groups. This study laid the foundation for the application of ReaxFF MD simulations to study the microscopic dynamic mechanism of SF\textsubscript{6} pyrolysis in more complex systems.

1. INTRODUCTION

Sulfur hexafluoride (SF\textsubscript{6}) has been widely used in gas-insulated equipment such as GIS and GIL due to its good insulation performance.\textsuperscript{1} Studies have shown that when a local overheating failure occurs in GIL equipment, SF\textsubscript{6} gas will decompose to produce SOF\textsubscript{4}, SO\textsubscript{2}F\textsubscript{2}, SOF\textsubscript{2}, SO\textsubscript{2}, HF, H\textsubscript{2}S, and other characteristic decomposition products.\textsuperscript{2–6} Since the type, content, and change rule of SF\textsubscript{6} overheating decomposition components are closely related to the internal overheating fault status of GIL equipment, the overheating fault status inside GIL can be effectively obtained by monitoring the content of these characteristic decomposition components.\textsuperscript{7} Considering that trace O\textsubscript{2} in the closed gas chamber has a great impact on the generation of oxygen-containing decomposition products, the GIL overheating fault diagnosis based on the SF\textsubscript{6} decomposition product analysis must consider the impact of trace O\textsubscript{2}. However, at present, the generation rules of SF\textsubscript{6} decomposition products and the generation mechanism of SF\textsubscript{6} oxygen-containing decomposition products under the influence of O\textsubscript{2} are still unclear. This is one of the key scientific problems that need to be solved urgently to apply the SF\textsubscript{6} decomposition component analysis method to monitor the internal overheating faults of GIS equipment.

At present, the research on the decomposition characteristics of SF\textsubscript{6} under the influence of trace O\textsubscript{2} is mainly focused on the decomposition phenomenon under discharge faults such as arc discharge, spark discharge, and partial discharge. Yang et al. studied the influence mechanism of O\textsubscript{2} content on the decomposition products of SF\textsubscript{6} under arc discharge.\textsuperscript{7} Tang et al. studied the influence of O\textsubscript{2} on the generation of SO\textsubscript{2}F\textsubscript{2} and SOF\textsubscript{2} in the case of partial discharge failures caused by metal protrusions.\textsuperscript{8} Lin et al. analyzed the sequence of chemical reactions during the formation of SF\textsubscript{6}-oxygenated decomposition products through an O isotope tracking method.\textsuperscript{9} There are relatively a few studies on the effect of O\textsubscript{2} on the decomposition characteristics of SF\textsubscript{6} under local overheating faults. Cheng et al. used the SF\textsubscript{6} thermal decomposition

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simulation experimental platform to study the influence of trace O₂ volume fraction on the main thermal decomposition products of SF₆.¹⁰ Wray et al. used a shock tube to study the oxidation of SF₆ and its decomposition products by O₂ and O atoms and proposed a mechanism according to the experimental results.¹¹ Tang et al. obtained the effect of trace O₂ on the effective gas production rate and the characteristic ratio of SF₆-overheated decomposition components through experiments and analyzed the influence mechanism of trace O₂ on the formation process of SF₆ overheated decomposition components.¹² However, due to the inherent limitations of the experimental platform, experimental operation process, and gas product detection technology, the results obtained in the experiment will inevitably be interfered by other factors, and it is difficult to grasp the full picture of the decomposition characteristics. In addition, since various factors have a very complicated influence mechanism on the chemical reaction process, the same product may be produced through completely different reaction mechanisms.⁹ Therefore, it is very arbitrary to use experimental results to speculate the reaction mechanism.

To grasp the decomposition mechanism more clearly, on the basis of experimental research, scholars have carried out research on the mechanism of O₂ participation in SF₆ decomposition based on quantum chemistry calculations. Fu et al. studied the formation pathways and reaction rate constants of SOF₆, SOF₄, SO₂F₂, and SO₂.¹³ Li et al. provided more detailed information including the data and energy structure of reaction intermediates and transition states.¹⁴ The conclusions obtained from these studies have important reference value for explaining the production mechanism of SF₆ products. However, these studies mainly use the analysis of the chemical bond strength and the energy change of the reaction system along the specific reaction path to determine the possible reaction path and the difficulty of the reaction. Such research cannot directly reflect the influence of temperature, gas pressure, and O₂ content on the decomposition mechanism of SF₆. Moreover, the dynamic process of decomposition and recombination in the actual chemical reaction process cannot be reproduced. According to the above analysis, it can be seen that through experiment and quantum chemical studies, the influence of O₂ on the formation of SF₆ decomposition products still has not been clearly grasped. Therefore, further research is needed.

Under such circumstances, a new research method that can overcome the shortcomings of the above methods is necessary. In recent years, molecular simulation methods have become an important scientific method to study the physical and chemical properties of materials.¹⁵ The reactive force field (ReaxFF), as a new type of force field, does not need to fix the connectivity between atoms, and the chemical bonds between atoms can form and dissociate freely. At the same time, its parameters come from the fitting of experimental data of the quantum mechanical method and still maintain the accuracy of quantum mechanical method calculations.¹⁶ So far, ReaxFF has been successfully applied in the field of molecular dynamics (MD) simulation of insulating gas.¹⁷,¹⁸ Using ReaxFF to simulate the pyrolysis process of SF₆ under the influence of trace O₂ has many advantages. For example, the scale of the simulation system can reach more than 1000 atoms, the research variables can be controlled accurately and flexibly in the simulation, and the simulation result contains the details of the molecular motion during the chemical reaction process, from which we can intuitively observe the way the chemical reaction occurs.

Currently, the challenge of using ReaxFF MD simulations to study the mechanism of O₂ participation in SF₆ pyrolysis is that there is no suitable force field to describe the molecular characteristics of a SF₆–O₂ system. To solve this problem, the ReaxFF force field for the SF₆–O₂ system is constructed and optimized in this paper. Then, a series of MD simulations were carried out based on the obtained force field. From a microcosmic point of view, the pyrolysis characteristics of SF₆ in a trace-oxygen (O₂) environment and the main product formation mechanism were analyzed. The research results in this article can provide theoretical support for a deep understanding of the microscopic mechanism of SF₆ overheated decomposition in the trace-oxygen (O₂) environment.

2. RESULTS AND DISCUSSION

2.1. Basic Decomposition Law of the SF₆–O₂ System.

In this work, we conduct MD simulations based on the optimized ReaxFF force field and then use the product curve obtained by MD simulations to study the basic decomposition law of the SF₆–O₂ system. Figures 1 and 2 show the product curves of the SF₆–O₂ system at 3500 and 4000 K, respectively.

![Figure 1. MD simulation results of the SF₆–O₂ system at 3500 K: (a) low-fluoride sulfides and (b) oxygen-containing byproducts.](https://dx.doi.org/10.1021/acsomega.0c03214)

It is found from Figure 1a that at a temperature of 3500 K, SF₆ is rapidly decomposed into various low-fluoride sulfides SFₓ (x = 1, 2, ..., 5). After 20 ps, the main components are (SF₄)⁺, (SF₃)⁺, and (SF₂)⁺. By observing the occurrence time of each product, it is found that (SF₄)⁺, (SF₃)⁺, (SF₂)⁺, and SF₂ appear in chronological order, indicating that SF₆ decomposes in consecutive steps down to SF₂. The dissociation energies of the S–F bonds in SF₆ and (SF₄)⁺ are 389.34 and 154.44 kJ/mol, respectively.¹⁹ Therefore, at a temperature that satisfies the decomposition of SF₆ (SF₄)⁺ can be easily decomposed into (SF₃)⁺. However, Figure 1a shows that the (SF₄)⁺ content continues to increase until it reaches the peak and then begins to decrease rapidly. To explain this phenomenon, we analyzed the main generation
paths of (SF₅)* in the MD process, as shown in eqs 1, 2, and 3, respectively:

\[ \text{SF}_6 = (\text{SF}_5)^* + \text{F}^* \]  
(1)

\[ (\text{SF}_5)^* + \text{SF}_6 = 2(\text{SF}_6)^* \]  
(2)

\[ (\text{SF}_5)^* + \text{F}^* = (\text{SF}_6)^* \]  
(3)

Combining these reaction paths with the product content in Figure 1a, it can be found that in the early stage of decomposition, the SF₆ content is high. The (SF₅)* generated by the decomposition of (SF₆)* can react with SF₆ to generate more (SF₅)*. At this time, the generation rate of (SF₅)* is greater than the consumption rate of (SF₆)*, so the (SF₅)* content gradually accumulates. As the reaction progresses, the SF₆ content in the system decreases, resulting in a decrease in the generation rate of (SF₆)*. After the (SF₅)* content reaches the maximum, the consumption rate of (SF₄)* exceeds its generation rate, resulting in the (SF₅)* content decreasing rapidly and remaining at a low level.

It can also be seen from Figure 1a that the time when (SF₄)* reaches the peak coincides with the time when (SF₅)* almost completely decomposes. After that, the (SF₅)* content decreases at a faster rate. This is because the bond energy of the S–F bond in (SF₅)* is similar to that of SF₆ and the (SF₅)* decomposition rate is faster than the (SF₆)* consumption rate. The rapid decomposition of (SF₅)* causes the accumulation of (SF₆)* content, reaching its peak. Comparing the slope of the (SF₅)* curve after the peak, it can be found that the decomposition rate of (SF₅)* is similar to that of SF₆ which is consistent with the experimental conclusion in the literature.³

From Figure 1b, it can be seen that O₂ starts to participate in the reaction at about 16 ps. The stable oxygen-containing byproducts produced are mainly SOF₂, SO₃F₂, SO₄F₂, etc., which are consistent with the results in the literature.⁵ Besides, it is found that among the oxygen-containing sulfur-fluoride compounds generated in the system, the content of (SOF₃)* is more than that of SOF₁₂, and only a small amount of SOF₄ is present.

The temperature has an important influence on chemical reactions. Studying the effect of temperature on the pyrolysis characteristics of the SF₆−O₂ system is a necessary way to understand the reaction mechanism. By comparing Figures 1 and 2, it is found that when the reaction temperature is further increased to 4000 K, the (SF₅)* content decreases and the (SF₆)* content increases. For oxygen-containing byproducts, the content of SOF₄ is further reduced, and at the same time, more (SOF₃)* decomposes into SOF₂, resulting in the SOF₂ content exceeding that of (SOF₄)*.

To verify the reliability of the MD simulation results, the relevant molecular bond dissociation energy calculated using quantum chemistry methods is shown in Table 1.

### Table 1. Bond Dissociation Energy

| molecule | bond | energy (kJ/mol) |
|----------|------|-----------------|
| SOF₄     | S=O  | 522.60          |
| SOF₂     | S=O  | 717.82          |
| SOF₄     | S−F  | 253.52          |
| SOF₂     | S−F  | 313.08          |
| O₂       | O=O  | 1024.72         |

From the data in Table 1, it can be seen that the dissociation energies of the S−F and S=O bonds in SOF₂ are 717.82 and 313.08 kJ/mol, respectively, while the dissociation energies of the S−F and S=O bonds in SOF₄ are only 253.52 and 522.60 kJ/mol, respectively. Therefore, compared with SOF₂, the thermal stability of SOF₄ is poor, and the higher reaction temperature makes the SOF₄ molecules in the system easy to lose F atoms and exist in the form of (SOF₃)* or SOF₂. It can be seen that the MD simulation results are consistent with the quantum chemical calculation conclusions.

### 2.2. Mechanism of O₂ Participating in the Reaction.

The mechanism of O₂ participating in the pyrolysis of SF₆ plays an important role in understanding the SF₆ pyrolysis characteristics under the trace-oxygen environment. To this end, we extracted more detailed information in the chemical reaction process from the MD simulation results at 3500 K, as shown in Figure 3.

According to Table 1, the dissociation energy of the O=O double bond in O₂ reaches 1024.72 kJ/mol, so it can be reasonably speculated that O₂ molecules are difficult to crack directly due to the high temperature. Comparatively speaking, O=O double bonds are more likely to be broken with the formation of other strongly exothermic chemical bonds. By tracing the behavior of O₂ molecules in the simulation process, it was found that almost no free O* appeared in the whole reaction process, which means that in the MD simulation process, reactions like O₂ = O* + O* or X + O₂ = XO + O* are not the main reaction pattern.

From Figure 3a,b, it can be seen that at around 11 ps, a small number of O₂ molecules began to combine with free F* to form unstable radical (O₂F)*. However, the temperature at this time is 2200 K, which is not sufficient to support further reactions. At about 16 ps, the system temperature reaches 3000 K. At this time, in addition to F*, many (SF₅)* and (SF₆)* radicals and a small amount of (SF₄)* were accumulated in the system. O₂ began to combine with (SF₅)* or (SF₆)* to form unstable radicals like (O₂SF₃)* or (O₂SF₄)*. For the above-mentioned radicals with unstable structures, the reverse reaction may occur soon after their formation, or they may further react to form new molecules, so their existence time is
Combining these phenomena observed from simulation results with previous inferences, we can conclude that the breaking of the O=O bond in O2 is because two O atoms in the O2 molecule form bonds with atoms in other highly reactive molecules or radicals. As a result, a transition structure like X(O2)Y is formed. The higher temperature provides enough energy to overcome the chemical reaction barrier. So, the O=O bond is degraded to an O−O single bond and then the single bond is broken, causing the two O atoms to enter different molecules or radicals.

According to the above analysis, it is found that when the SF6−O2 system decomposes due to overheating, O2 rarely generates free O atoms by self-cracking. While according to the existing research, in the discharge environment, electron bombardment will promote the cleavage of O2 molecules into free O atoms. Since the reaction activity of O atoms and O2 molecules is very different, under the two types of fault conditions of overheating and discharge, the decomposition reaction mechanism of SF6 is theoretically different. Therefore, at least for SF6 in the trace-oxygen environment, the discharge conditions cannot be simply summarized from the perspective of energy as the influence of temperature. Considering that, in practical applications, the decomposition of SF6 gas is more likely to be caused by a certain discharge fault, the specific reaction mechanism for the SF6−O2 system in the discharge environment still needs further study.

2.3. Generation Paths Analysis of Main Products. To further study the formation mechanism of various oxygen-containing sulfur-fluoride compounds, the main generation path of these compounds was obtained by analyzing the trajectory of atoms during MD simulations, as shown in Table 2.

### Table 2. Main Generation Paths of the Target Products in the Simulation Process

| products | generation path | path ID |
|----------|-----------------|---------|
| SOF4     | O2 + (SF3)* + (SF3)* = SOF4 + (SOF3)* | (1)     |
|          | (SOF3)* + F* = SOF4 | (2)     |
| SOF2     | O2 + (SF2)* + (SF2)* = SOF2 + (SOF3)* | (3)     |
|          | (SOF2)* = SOF2 + F* | (4)     |
|          | (SOF)* + F* = SOF2 | (5)     |
| SOF3     | O2 + (SF3)* + (SF3)* = SOF3 + (SOF3)* | (6)     |
|          | O2 + (SF2)* + (SF2)* = SOF2 + SOF4 | (7)     |
| SOF2     | O2 + (SF2)* + F* = SOF2 + (OF)* | (8)     |
| SO2F2    | (SO2F2)* + F* = SO2F2 | (9)     |
| SOF5     | (SOF)* + O2 = SO2F2 | (10)    |

It can be seen from Table 2 that the typical reaction mode of O2 participating in the SF6 pyrolysis process is X + Y + O2 = XO + YO. (SOF3)* is an important intermediate product connecting SOF2 and SOF4. In addition, according to the decomposition rule of SF6 in Figure 1, SF6 has been completely decomposed before O2 participates in the reaction. So O2 does not directly react with SF6.

To verify the reliability of the reaction paths with O2 participation obtained by MD simulations, the standard reaction enthalpy of a series of reactions was calculated by quantum chemistry methods, as shown in Table 3.

According to the standard reaction enthalpy data in Table 3, it is possible to roughly infer the degree of difficulty of the same type of reaction under the same condition of reactant concentration, temperature, etc. For example, reaction paths...
A2 and A3 are more likely to occur than reaction path A1. Comparing the results in Table 2, it is found that the main reaction paths observed in the MD process are all exothermic reactions with relatively large absolute values of the standard reaction enthalpy, so the quantum chemistry calculation results are basically consistent with the MD simulation results.

In addition, from the data in Table 3, it can be seen that the order of reactivity of various groups to O2 is (SF3)* > (SF4)* > (SF2)* > F*, so O2 is more likely to generate oxygen-containing byproducts by attacking (SF3)* and (SF4)* groups, which is consistent with the conclusion of the literature.

It is worth noting that for reaction C, 2(SF2)* + O2 = 2SOF2, the standard reaction enthalpies are -410.933 kJ/mol. According to the reaction enthalpy, it can be speculated that this reaction is easy to occur, but no corresponding reaction is observed during the MD process. This is because, in a closed MD system, the F* generated by decomposition cannot diffuse into the surrounding space. The accumulation of a large number of free F atoms in the system will inhibit the further decomposition of SF6, which results in a low content of (SF2)* in the system and less chance of its contact with O2. This phenomenon will cause deviations between the simulation results and the actual measurement results, which is an inherent defect of the closed-system MD simulation.

3. CONCLUSIONS

According to the work done in this paper, the innovative research results obtained mainly include the following:

1. The ReaxFFSFO reactive force field that accurately describes the properties of the SF6-O2 system was constructed and optimized, and the reliability of the ReaxFFSFO force field was verified from multiple dimensions. Then, the MD simulation results are compared with the experimental results and quantum chemistry calculation results, which proves the reliability of using ReaxFF to study the pyrolysis mechanism of the SF6-O2 system.

2. The main oxygen-containing byproducts generated in the MD simulation are SOF2, SOF3, and SO2F2, which are basically consistent with the experimental conclusions in the literature. The basic mode of O2 participating in a chemical reaction is X + Y + O2 = XO + YO, with a relatively large absolute value of the standard reaction enthalpy. This mechanism may be very different from the decomposition mechanism under discharge conditions.

3. The order of reactivity of various groups to O2 is (SF3)* > (SF4)* > (SF2)* > F*. So, O2 is more likely to generate oxygen-containing byproducts by attacking (SF3)* or (SF4)* groups. The thermal stability of SOF2 is stronger than that of SOF4. As the reaction temperature increases, the content of SOF2 in the system increases and the content of SOF4 decreases. The quantitative relationship between the two products can be used to determine the fault temperature.

There are also some limitations in using ReaxFF MD simulations to study the decomposition mechanism of SF6 in the trace-oxygen environment. Accordingly, we have proposed some possible solutions.

1. ReaxFF does not support discharge parameters, so it cannot be used to directly study the decomposition mechanism of SF6-O2 in the discharge environment. To solve this problem, we could use O3 molecules, which have a lower decomposition temperature, to introduce an appropriate amount of O atoms into the reaction system, so as to simulate the cracking of O2 molecules due to electron bombardment in the discharge environment.

2. To avoid the negative effects caused by excessive F* accumulation mentioned in Section 2.3, we could periodically remove part of the F* atoms generated by the reaction to simulate the phenomenon of F* spreading to the surrounding space, thereby more accurately describing the microscopic dynamic mechanism during local overheating failure in GIL.

We hope that the research results of this work can provide a reference for a deeper understanding of the SF6 pyrolysis mechanism in the trace-oxygen environment. More importantly, we also hope this article can provide a brand-new idea for studying the mechanism of trace-oxygen or trace-water participating in SF6 decomposition.

4. OPTIMIZATION AND SIMULATION METHODS

4.1. Force Field Construction and Optimization.

Similar to the traditional empirical force field, the ReaxFF reactive force field represents the system energy as the sum of the energy of multiple parts, taking into account the effects of van der Waals and Coulomb forces. The energy expression is shown in eq 4.16

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWals} + E_{Coulomb}$$

ReaxFF can directly reflect the microscopic dynamic process when a chemical reaction occurs and thus has important reference value for understanding the reaction mechanism.

In the existing force fields containing S, F, and O elements, the force field parameters related to S, F, and O are all missing or invalid. Therefore, before optimizing the force field parameters, it is necessary to construct a reasonable force field parameter structure according to the actual situation of the SF6-O2 system. To this end, we have completed the bond, angle, off-diagonal, and torsional angle force field parameter terms related to SFO to construct the ReaxFFSFO initial force field.
In this paper, the ReaxFF\textsubscript{SF6} force field is optimized based on the density functional theory (DFT) calculation results. To accurately describe the geometry structure and energy state of important molecules and transition states in the SF\textsubscript{6}−O\textsubscript{2} system, we analyzed the molecules that may appear in the SF\textsubscript{6}−O\textsubscript{2} system and then added SF\textsubscript{x}, SOF\textsubscript{2}, SOF\textsubscript{4}, SO\textsubscript{2}F\textsubscript{2}, SO\textsubscript{2}, O\textsubscript{2}, OF\textsubscript{2}, etc. in the training set. The training set composition is shown in Table 4. The final training set composition is shown in Table 4.

Table 4. Composition of the Training Set

| number of items | bond length | bond angle | energy |
|----------------|-------------|------------|--------|
| 50             | 87          | 2100       |

Due to the complex coupling relationship between the parameters, the quality of the initial force field has some positive influence on the optimization results.\textsuperscript{21} Therefore, we conducted multiple preoptimizations starting from random initial parameters and used the force field with the smallest error as a credible start. Considering that this force field will be used to study the characteristics of the pyrolysis chemical reaction of the SF\textsubscript{6}−O\textsubscript{2} system, in the process of force field optimization, more attention has been paid to the changes in molecular energy, and the weight of the energy term has been appropriately increased.

At present, the commonly used methods of force field parameter optimization include the Monte Carlo (MCFF) algorithm and covariance matrix adaptation evolution strategy (CMA-ES) algorithm. The MCFF method has a better effect of optimizing near the global optimal area, but the effect of searching the global optimal solution from a random initial position is poor. Therefore, to use the MCFF method for optimization, an appropriate initial force field must be given. The CMA-ES method has a relatively fast local optimal convergence speed, but it is also easy to fall into the local optimal trap and lose sensitivity to the weight parameters, thereby hindering further optimization of the parameters. Based on the above analysis, in this article, MCFF and CMA-ES algorithms are combined to optimize the ReaxFF\textsubscript{SF6} force field. After continuous trial and adjustment, the desirable ReaxFF\textsubscript{SF6} force field was finally obtained.

4.2. Force Field Reliability Verification. To verify the reliability of the optimized ReaxFF\textsubscript{SF6} force field, we analyzed the deviation between the results calculated using the force field and the reference value from the training set. The statistical results are shown in Figure 5.

It can be seen from Figure 5a, b that the fitting deviations of the reaction force field to the molecular bond length and bond angle are mainly concentrated within ±5%, so it is believed that the force field can well reproduce the molecular geometry.\textsuperscript{16,22} For the case where the calculation error distribution of bond length and bond angle is not continuous, this is because the numbers of bond length (50) and bond angle (87) terms considered in the training set of this article are relatively small. In addition, when optimizing the force field parameters, more attention is paid to the fitting effect of the energy, so the weight of the energy term is increased, which indirectly affects the fitting accuracy of the force field to the bond length and bond angle parameters. For the application scenarios in this article, the fitting accuracy of the bond length and bond angle can meet the application requirements.

It can be seen from Figure 5c that the fitting error of molecular energy near 0 kJ/mol accounts for the highest proportion and the fitting error within ±20 kJ/mol accounts for 74.8%. Therefore, it is believed that this force field can well reproduce the quantum chemical energy parameters of molecules.\textsuperscript{16,22} The larger energy deviation observed in Figure 5c mainly comes from the bond dissociation energies of SF\textsubscript{6}, (SF\textsubscript{5})\textsuperscript{−}, and (SF\textsubscript{4})\textsuperscript{−}, which will be further explained later.

In summary, the ReaxFF\textsubscript{SF6} force field has good overall performance in describing the molecular characteristics, especially energy. In addition to the overall performance, we still need to pay attention to the description accuracy of key
molecules by the ReaxFF_{SO} force field. Some typical geometric parameters and bond dissociation energy of key molecules are shown in Table 5 and Figures 6 and 7.

| molecular name | bond angle (deg) | ReaxFF | DFT | error (%) |
|----------------|-----------------|--------|-----|-----------|
| SF₆            | S₁−F₂           | 1.6027 | 1.6105 | −0.48     |
|                | F₂−S₁−F₃       | 90.0830 | 90.0000 | 0.09      |
| (SF₄)*         | S₁−F₂           | 1.6039 | 1.6976 | −5.52     |
|                | F₂−F₃           | 1.5849 | 1.6071 | −1.38     |
|                | F₂−S₁−F₃       | 87.9264 | 88.2000 | −0.31     |
|                | F₂−S₁−F₄       | 173.5413 | 174.5000 | −0.55     |
|                | F₃−S₁−F₅       | 99.8671 | 100.6000 | −0.73     |
| SOF₄           | S₁−O₄           | 1.4347 | 1.4278 | 0.48      |
|                | S₁−F₅           | 1.5864 | 1.6307 | −2.72     |
|                | F₂−S₁−F₃       | 85.6996 | 84.0000 | 2.02      |
|                | F₂−S₁−F₄       | 148.3431 | 142.3000 | 4.25     |
|                | F₂−S₁−O₆       | 105.8276 | 108.9000 | −2.82     |
| SOF₅           | S₁−O₄           | 1.4440 | 1.4472 | −0.22     |
|                | S₁−F₂           | 1.5558 | 1.6498 | −5.70     |
|                | F₂−S₁−F₃       | 86.2586 | 93.4000 | −7.64     |
|                | F₂−S₁−O₄       | 108.5738 | 106.9000 | 1.57     |
| SOF₂           | S₁−O₃           | 1.4517 | 1.4319 | 1.38      |
|                | S₁−F₅           | 1.5645 | 1.5949 | −1.91     |
|                | F₂−S₁−F₃       | 85.9035 | 95.2000 | −9.77     |
|                | F₂−S₁−O₄       | 110.4315 | 107.9000 | 2.35     |
|                | O₅−S₁−O₄       | 123.8648 | 125.7000 | −1.46     |

Table 5. Comparison of Geometric Parameters of Key Molecules in the SF₆−O₂ System

“A−B represents the bond length between A and B atoms, A−B−C represents the angle ABC formed by three atoms, and the subscript numbers are the atom numbers.

It can be seen from Table 5 that the deviation of molecular geometric parameters between ReaxFF and DFT calculation results is mainly concentrated within ±5%, which means that the force field is reliable for describing key molecular geometry. We noticed that the S−F bond lengths in the (SF₄)* and SOF₂ molecules calculated by ReaxFF have relatively large deviations from the DFT calculation results. This is because the S−F bond lengths of most molecules in the training set are distributed around 1.6 Å, resulting in the equilibrium distance of the S−F bond in the optimal force field being close to 1.6 Å. Therefore, for the longer S−F bond lengths in the (SF₄)* and SOF₂ molecules, the calculation deviation is relatively large. In addition, it can be found that in the SOF₂ and SOF₂ molecules, the F−S−F bond angle deviation is large than average. This is because in the optimization process, to maintain the unique seesaw-shaped structure of the (SF₄)* molecule (rather than the regular tetrahedral structure), we increase the fitting weight of the (SF₄)* bond angle term, which indirectly affects the fitting accuracy of the F−S−F bond angle of SOF₂ (triangular pyramid-like structure) and SOF₂ (tetrahedral-like structure) molecules. Although the force field has a relatively large error in fitting some molecular parameters, in general, the ReaxFF force field optimized in this paper can reproduce the molecular geometry of the SF₆−O₂ system well.

It can be seen from Figure 6 that near the equilibrium point, the force field fits the S−F bond energy in SF₆ (SF₄)*, and (SF₄)* with high accuracy. However, when the bond length increases to a certain extent, the calculation result of ReaxFF will deviate from the calculation result of DFT. This is because the SF₆ and (SF₄)* bond dissociation energy is larger and close to each other, while the (SF₄)* bond dissociation energy is relatively small. ReaxFF uses the same set of parameters to describe the interaction relationship between S and F atoms, therefore, the ReaxFF calculation results of the S−F bond energy in different molecules are compromised. Specifically, the ReaxFF calculation results of the S−F bond dissociation energy in SF₆ and (SF₄)* is smaller than the DFT calculation results, while the ReaxFF calculation result of the S−F bond dissociation energy in (SF₄)* is larger than the DFT calculation result. Nevertheless, the ReaxFF force field has successfully reproduced the bond dissociation energy relationship of key molecules such as SF₆ (SF₄)*, and (SF₄)*, so it can accurately describe the thermal decomposition process of SF₆. In addition, the results in Figure 7 show that this force field has a satisfactory description accuracy for the S−F and S=O bond energies in SOF₂.
 Furthermore, the thermal stability of SF$_6$ in the temperature range of 300−1000 K was verified in a series of MD simulations. The results show that the thermal stability of SF$_6$ in the ReaxFF$_{SF6}$ force field is basically consistent with the experimental conclusion.$^{23}$

In summary, the reliability validation results of the force field in multiple dimensions indicate that the ReaxFF$_{SF6}$ force field can accurately describe the properties of various molecules in the SF$_6$−O$_2$ system. Thus, it is quite reasonable to study the microscopic dynamic mechanism of the chemical reactions in the SF$_6$−O$_2$ system based on the ReaxFF$_{SF6}$ force field.

4.3. MD Simulation Method of the SF$_6$−O$_2$ System. The pressure range of SF$_6$ in gas-insulated equipment is generally 0.2−0.5 MPa.$^1$ To study the thermal decomposition characteristics of SF$_6$ in the trace-oxygen environment, a box filled with 80 SF$_6$ molecules and 10 O$_2$ molecules was constructed, as shown in Figure 8. We adjust the size of the box to make the gas pressure at room temperature equivalent to 0.4 Mpa. This study uses the ReaxFF module of AMS software for MD simulations. All simulations involved in this paper use the NVT ensemble. The temperature control method is Berendsen, and the simulation time step is 0.25 fs. The ReaxFF$_{SF6}$ optimized by this paper is used as the force field.

Before the start, a series of presimulations were first performed. The results show that SF$_6$ can exist stably under 700 K and start to decompose around 1000 K. O$_2$ begins to participate in the reaction at a desirable reaction rate around 3000 K. Based on the presimulation results, the reaction temperatures were set to 3500 and 4000 K. After 5000 steps of relaxation at 298 K, the system temperature was gradually increased at a rate of 0.2K/fs until the target temperature was reached. A total of 400 000 steps were performed for a total of 100 ps MD simulation.

In this paper, during the analysis of some MD simulation results, the DFT calculation data is used as a reference.$^{24}$ Several previous works show that theoretical studies based on DFT with the use of B3LYP functional are available for SF$_6$ and its main decomposition byproducts including SF$_x$, SOF$_2$, SOF$_4$, etc.$^{13,25,26}$ The Gaussian 09 package was used to investigate the decomposition mechanism of SF$_6$ in the trace-O$_2$ environment with the DFT-B3LYP/6-311+G(d,p) quantum chemistry method.$^{19}$

### Figure 7.
Comparison of bond dissociation energy calculated by ReaxFF and DFT: (a) S−F bond dissociation energy in SOF$_4$ and (b) S≡O bond dissociation energy in SOF$_4$.

![Figure 7. Comparison of bond dissociation energy calculated by ReaxFF and DFT: (a) S−F bond dissociation energy in SOF$_4$ and (b) S≡O bond dissociation energy in SOF$_4$.](https://dx.doi.org/10.1021/acsomega.0c03214)

### Figure 8.
Structure of the SF$_6$−O$_2$ system.

![Figure 8. Structure of the SF$_6$−O$_2$ system.](https://dx.doi.org/10.1021/acsomega.0c03214)

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**Notes**

The authors declare no competing financial interest.

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REFERENCES

(1) Mazzanti, G.; Stomeo, G.; Mancini, S. State of the art in insulation of gas insulated substations: main issues, achievements, and trends. IEEE Trans. Dielectr. Electr. Insul. Mag. 2016, 32, 18–31.
(2) Chu, F. Y. SF₆ Decomposition in Gas-Insulated Equipment. IEEE Trans. Dielectr. Electr. Insul. 1986, 21, 693−725.
(3) Chu, F. Y.; Massey, R. E. Thermal Decomposition of SF₆ and SF₆-Air Mixtures in Substation Environments. In Gaseous Dielectrics III; Christophorou, L. G., Ed.; Pergamon, 2013; pp 410−419.
(4) Cui, H.; Zhang, X.; Zhang, J.; Zhang, Y. Nanomaterials-based gas sensors of SF₆ decomposed species for evaluating the operation status of high-voltage insulation devices. High Voltage 2019, 4, 242−258.
(5) Zeng, F.; Tang, J.; Zhang, X.; Sun, H.; Yao, Q.; Mao, Y. Study on the Influence Mechanism of Trace H₂O on SF₆ Thermal Decomposition Characteristic Components. IEEE Trans. Dielectr. Electr. Insul. 2015, 22, 766−774.
(6) Cui, H.; Yan, C.; Jia, P.; Cao, W. Adsorption and sensing behaviors of SF₆ decomposed species on Ni-doped C₃N monolayer: A first-principles study. Appl. Surf. Sci. 2020, 512, No. 145759.
(7) Yang, R.; Xu, M.; Guan, C.; Yan, J.; Geng, Y. Influence of trace H₂O and O₃ on SF₆ decomposition products under arcing conditions in electric power equipment. J. Eng. 2019, 2019, 1774−1777.
(8) Tang, J.; Yang, D.; Zeng, F.; Zhang, X. Research Status of SF₆ Insulation Equipment Fault Diagnosis Method and Technology Based on Decomposed Components Analysis. Trans. China Electrotech. Soc. 2016, 31, 41−54.
(9) Lin, T.; Han, D.; Zhang, G.; Liu, D. Influence of Trace O₂ on SF₆ Decomposition Characteristics under Partial Discharge based on Oxygen Isotope Tracer. IEEE Trans. Dielectr. Electr. Insul. 2017, 24, 1600−1607.
(10) Cheng, L.; Peng, F.; Tang, J.; Wang, L.; Yao, Q.; Zeng, F. Action Mechanism of Trace O₂ on Characteristic Components of SF₆ Thermal Decomposition. High Voltage 2015, 41, 4105−4112.
(11) Wray, K. L.; Feldman, E. V. The pyrolysis and subsequent oxidation of SF₆. Symp. (Int.) Combust. 1973, 14, 229−238.
(12) Tang, J.; Huang, X.; Zeng, F.; Sun, H. Influence Analysis of Trace O₂ on the Forming Process of SF₆ Overthermal Decomposition Components. Proc. CSEE 2015, 35, 2617−2624.
(13) Fu, Y.; Rong, M.; Yang, K.; Yang, W.; Wang, X.; Gao, Q.; Liu, D.; Murphy, A. B. Calculated rate constants of the chemical reactions involving the main byproducts SO₂F, SOF₂, SO₂F₂ of SF₆ decomposition in power equipment. J. Phys. D: Appl. Phys. 2016, 49, No. 155502.
(14) Li, Z.; Chen, S.; Gong, S.; Feng, B.; Zhou, Z. Theoretical study on gas decomposition mechanism of SF₆ by quantum chemical calculation. Comput. Theor. Chem. 2016, 1088, 24−31.
(15) Lu, X.; Wang, X.; Li, Q.; Huang, X.; Han, S.; Wang, G. A ReaxFF-based molecular dynamics study of the pyrolysis mechanism of polyimide. Polym. Degrad. Stab. 2015, 114, 72−80.
(16) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: A Reactive Force Field for Hydrocarbons. J. Phys. Chem. A. 2001, 105, 9396−9409.
(17) Li, Y.; Zhang, X.; Xiao, S.; Chen, Q.; Tang, J.; Chen, D.; Wang, D. Decomposition Properties of C4F7N/N2 Gas Mixture: An Environmentally Friendly Gas to Replace SF₆. Ind. Eng. Chem. Res. 2018, 57, 5173−5182.
(18) Li, Y.; Zhang, X.; Tian, S.; Xiao, S.; Li, Y.; Chen, D. Insight into the decomposition mechanism of C₆F₁₂O−CO₂ gas mixture. Chem. Eng. J. 2019, 360, 929−940.
(19) Zhong, L.; Ji, S.; Wang, F.; Sun, Q.; Chen, S.; Liu, J.; Hai, B.; Tang, L. Theoretical study of the chemical decomposition mechanism and model of Sulfur hexafluorid (SF₆) under corona discharge. J. Fluorine Chem. 2019, 220, 61−68.
(20) Mueller, J. E.; van Duin, A. C. T.; Goddard, W. A. Application of the ReaxFF Reactive Force Field to Reactive Dynamics of Hydrocarbon Chemisorption and Decomposition. J. Phys. Chem. C 2010, 114, 5675−5685.
(21) Shchygol, G.; Yakovlev, A.; Trmka, T.; van Duin, A. C. T.; Verstraeten, T. ReaxFF Parameter Optimization with Monte-Carlo and Evolutionary Algorithms: Guidelines and Insights. J. Chem. Theory Comput. 2019, 15, 6799−6812.
(22) Liu, Y.; Hu, J.; Hou, H.; Wang, B. Development and application of a ReaxFF reactive force field for molecular dynamics of perfluoroketones thermal decomposition. Chem. Phys. 2020, 538, No. 110888.
(23) Zeng, F.; Tang, J.; Fan, Q.; Pan, J.; Zhang, X.; Yao, Q.; He, J. Decomposition characteristics of SF₆ under thermal fault for temperatures below 400 °C. IEEE Trans. Dielectr. Electr. Insul. 2014, 21, 995−1004.
(24) Wang, J.; Li, Q.; Liu, H.; Huang, X.; Wang, J. Theoretical and experimental investigation on decomposition mechanism of eco-friendly insulation gas HFO1234zeE. J. Mol. Graphics Modell. 2020, 100, No. 107671.
(25) Lobring, K. C.; Catherine, E. C.; Thomas, M. G.; Lee, S. S. New measurements of the thermochemistry of SF₆⁺ and SF₆⁻. Int. J. Mass Spectrom. 2003, 227, 361−372.
(26) Buendia-Atencio, C.; Gilles, P. P.; Adela, E. C.; Carlos, J. C. Theoretical kinetic study of the reaction of SF₆ radical with F₂, Cl₂ and SF₆. Comput. Theor. Chem. 2016, 1090, 41−46.