

Analysis of the Molecules Structure and Vertical Electron Affinity of Organic Gas Impact on Electric Strength*

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Abstract It is necessary to find an efficient selection method to pre-analyze the gas electric strength from the perspective of molecule structure and the properties for finding the alternative gases to sulphur hexafluoride (SF_6). As the properties of gas are determined by the gas molecule structure, the research on the relationship between the gas molecule structure and the electric strength can contribute to the gas pre-screening and new gas development. In this paper, we calculated the vertical electron affinity, molecule orbits distribution and orbits energy of gas molecules by the means of density functional theory (DFT) for the typical structures of organic gases and compared their electric strengths. By this method, we find part of the key properties of the molecule which are related to the electric strength, including the vertical electron affinity, the lowest unoccupied molecule orbit (LUMO) energy, molecule orbits distribution and negative-ion system energy. We also listed some molecule groups such as unsaturated carbons double bonds ($\text{C}=\text{C}$) and carbonitrile bonds ($\text{C}\equiv\text{N}$) which have high electric strength theoretically by this method.

Keywords: gas insulation, electric strength, SF_6 substitutes, molecule structure

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(Some figures may appear in colour only in the online journal)

1 Introduction

Sulphur hexafluoride (SF_6) is widely used in gas-insulated power equipment. Due to the excellent qualities including insulating performance, being non-toxic, nonflammable and having a low boiling point, SF_6 can be used in many different conditions and equipment. However, with its high global warming potential (GWP), the use of SF_6 has been restricted in Kyoto Protocol [1]. Many researches and experiments have been done to find substitute gases and gas mixtures for SF_6 [2–5]. So far we have not found a perfect substitute gas which can be applied in all the electrical equipment to replace SF_6 .

A very large database of candidate gases is necessary to find an alternative gas which meets the qualities including high electric strength, non-toxic and low GWP. Since organic gases have a variety of structures and element components, there are thousands of organic gases which can form a gas selection database and the alternative gas to SF_6 is most likely an organic gas. So in this paper we focused on the organic gases with basic molecule structures and listed some basic relationships between microscopic properties and electric strength.

By the previous studies, there are three dimensions

of methods to measure the gas electric strength, phenomenological, macroscopic and microscopic [6]. For the phenomenological dimension, many breakdown experiments, such as the needle-plane test, should be done to qualify the electric strength in different gas pressures and different electrical fields. This method is most comprehensive and accurate. However, it is inefficient and requires a lot of gas material. So it is suitable for in-depth study of certain gases. Some potential alternative gases such as octafluorocyclobutane ($\text{c-C}_4\text{F}_8$) and iodotrifluoromethane (CF_3I) have been tested by breakdown experiments and parts of them have the potential to replace SF_6 in some characteristics [7–9]. However, they all have their own disadvantages for application such as the high GWP for $\text{c-C}_4\text{F}_8$ and the high boiling point and price for CF_3I , which means we still need to find new substitute gases [10]. For the macroscopic and microscopic dimension, the Monte Carlo method and Boltzmann equations are often used to calculate the electron transport parameters. L. G. Christophorou and M. C. Bordage analyzed the electron swarm parameters and electron interactions of CF_4 by the Boltzmann method [11,12]. Y. K. Deng calculated effective ionization coefficients and electron drift velocities, and then analyzed the insulating character-

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istics of $c\text{-C}_4\text{F}_8$ gas mixtures and CF_3I gas mixtures by Boltzmann equation analysis [13–15]. Y. Wu and H. Sun also used the Boltzmann equation to predict the critical dielectric strength of CF_4 and CO_2 in high temperature and analyzed their applications in the circuit breaker [16,17]. This method can help to calculate the dielectric strength of gases in different pressures, different mixing rates or different temperatures; however, it is necessary to measure the cross-section data before. So the Boltzmann method is suitable for measuring the gases with known parameters rather than pre-screening [18].

Besides the three dimensions to measure electric strength, there is a theory computing method with the means of quantum mechanics on gas molecule properties. This is one of the most fundamental ways to qualify the gases dielectric performance. This method only needs the chemical formula and general structure of gas rather than other electric parameters. With the known gas chemical formula the molecular structure will be optimized for the most likely result and the molecule microscopic properties and parameters such as vertical electron affinity and molecule orbits distribution which can be used to analyze the electric strength will be calculated. Density functional theory (DFT) has provided support to this method, which makes it possible to reduce the cost of computing to form a highly efficient gas electric strength estimation method for screening gases [19]. The study can also lead to a deeper understanding of the relationship between molecule structure and insulation [20,21].

In this paper, section 2 describes the computational methods of molecular vertical electron affinity and orbits energy by the means of DFT. In section 3 we list part of saturated and unsaturated hydrocarbons, saturated and unsaturated fluorocarbons vertical electron affinities and their electric strengths. Then we analyzed the relationship between their vertical electron affinities and molecular orbital energy. In addition, we listed some fluoro-nitrile organic gases as potential substitutes for SF_6 by this method.

2 Method

The gas insulation is actually to limit the free electrons in a relatively low energy level as a barrier. There are several processes between gas molecules and electrons, such as electron collision ionization processes, electron attachment processes, electron diffraction processes and interruption processes [6]. From the molecule aspect, the insulation gas should have the tendency to attach free electrons rather than to lose electrons or ionize. Vertical electron affinity is the energy difference between negative ion and neutral molecule of insulation gas. The lower vertical electron affinity can lead to a tendency to absorb electrons and a high electron-attachment capacity. The lowest unoccupied molecular orbits (LUMO), which are for the attached electrons,

also have a great relationship with the electron attachment. So in this paper we focus on the vertical electron affinity and LUMO calculations.

Taking into account the industrial application conditions, insulating gases should have a low boiling point. So in this study, the organic gases molecules contain no more than 4 carbon atoms to make sure the boiling points are 0° below. We build the molecule structures by parametric model 3 (PM3) semi-empirical methods [21,22]. Then we optimized the molecule model and calculated the system energy by means of DFT. For the computing setting, we chose the Becke-style 3-parameter density functional theory (B3LYP) model, which leads to a relatively accurate result and an inexpensive process [23]. The exchange-correlation functional that was devised by Becke in 1993 is

$$E_{xc}^{\text{B3}} = A \cdot E_x^{\text{Slater}} + (1 - A) \cdot E_x^{\text{HF}} + B \cdot \Delta E_x^{\text{Becke}} + E_c^{\text{VWN}} + C \cdot \Delta E_c^{\text{non-local}}. \quad (1)$$

Here the E_x is for the exchange functional and the E_c is for the correlation functional [24]. Slater, HF (Hartree-Fock) and VWN (Vosko-Wilk-Nusair) are for the different forms of exchange energy or correlation. $\Delta E_x^{\text{Becke}}$ is for the Becke's gradient correction for exchange. A , B and C are the semi-empirical coefficients. The hybrid functional B3LYP uses the LYP (Lee-Yang-Parr) expression in non-local correlation and the LYP contains both local and non-local terms while the VWN is for local correlation here. Then the functional B3LYP can be [25]

$$E_{xc}^{\text{B3LYP}} = A \cdot E_x^{\text{Slater}} + (1 - A) \cdot E_x^{\text{HF}} + B \cdot \Delta E_x^{\text{Becke}} + C \cdot E_c^{\text{LYP}} + (1 - C) \cdot E_c^{\text{VWN}}. \quad (2)$$

For the basis sets, we chose the polarized basis set 6-31G(d), which has a d function compared to 6-31G. The 6-31G(d) is a common calculation basis set for medium size systems.

For the molecules, due to the fact that they are electrically neutral, the spin multiplicity is 1. For the negative ions, the total charge is -1 and the spin multiplicity is 2. As during the electron collision processes, the gas molecules may re-form a new molecule or ion, this paper only analyzes the situation with one free electron attachment [26].

In order to quantify the molecules electron adsorption and attraction, we use electron cloud distribution to qualify the molecule volume. Molecule volume is calculated by the Monte Carlo method, according to the Bader definition of van der Waals volume with the criteria of electron surface density being $0.0001/\text{Bohr}^2$.

3 Results and discussion

For the research of organic gases, we start from the saturated and unsaturated hydrocarbons such as methane, ethane, ethylene, and propylene which have

the basic structure and elements components. Due to their instability and flammability, these gases cannot be used as insulating gases, but their microscopic properties can still be good bases for research. In Table 1, we list the vertical electron affinity and computing molecule volumes of them.

Table 1. Vertical electron affinity and molecule volumes of hydrocarbons

	Vertical electron affinity (Hartree)	Molecule volumes (Bohr ³)
Methane (CH ₄)	0.1943	279.419
Ethane (C ₂ H ₆)	0.1760	441.982
Ethylene (C ₂ H ₄)	0.1112	380.382
Propane (C ₃ H ₈)	0.1630	597.509
Propylene (C ₃ H ₆)	0.1009	540.954
N-butane (N-C ₄ H ₁₀)	0.1600	752.710
1-Butene (1-C ₄ H ₈)	0.0966	702.169
1,3-Butadiene (1,3-C ₄ H ₆)	0.0517	640.759

From the results we can see that the unsaturated hydrocarbons have much lower vertical electron affinity compared with the saturated molecules with the same number of carbon atoms. While because of the double bonds (C=C) being shorter than the single bonds (C-C), the volumes of unsaturated hydrocarbons are relatively smaller. Based on J. C. Devins test results, the electric strengths are enhanced with the number of carbon atoms increasing in similar structure molecules, which is partly because of the greater molecule size [27]. In A. E. D. Heylen and T. J. Lewis tests, the electric strengths of unsaturated hydrocarbons are much higher than saturated ones, which is contrary to the trend of volume change [28,29]. The electric strength and vertical electron affinity trends are shown in Fig. 1. Besides the impact of volume, we find the electric strength has a significant negative correlation with vertical electron affinity. Table 2 shows the LUMO energy of them, which are calculated with the B3LYP method and 6-31G(*d*) basis sets. A lower LUMO energy of a molecule means the free electrons can be attached more easily. In Fig. 2 the LUMO energy and vertical electron affinity show a good linear relationship. That is to say the LUMO has a significant effect on the vertical electron affinity. The deviation of C₂H₄ may be because the structures difference that C₂H₄ only have one double bond and no single bond. Fig. 3 is the comparison of orbits distribution between C₃H₈ and C₃H₆. Fig. 4 is

Table 2. LUMO energy of hydrocarbons

	LUMO energy (Hartree)
Methane (CH ₄)	0.11786
Ethane (C ₂ H ₆)	0.10477
Ethylene (C ₂ H ₄)	0.01881
Propane (C ₃ H ₈)	0.09607
Propylene (C ₃ H ₆)	0.02835
N-butane (N-C ₄ H ₁₀)	0.09489
1-Butene (1-C ₄ H ₈)	0.02588
1,3-Butadiene (1,3-C ₄ H ₆)	-0.0225

the LUMO distribution simulation of C₃H₆. As shown in Fig. 4, the LUMO is around the double bond and the double bond has better qualities for reducing vertical electron affinity and leading to a better electric strength.

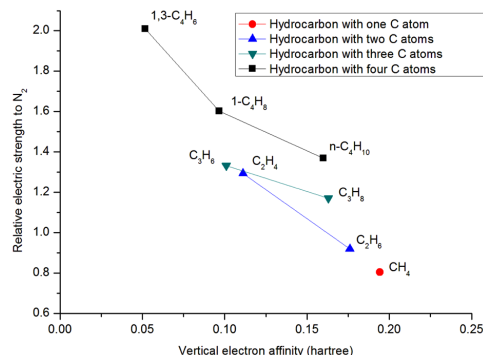


Fig.1 Relative electric strength and vertical electron affinity of hydrocarbons

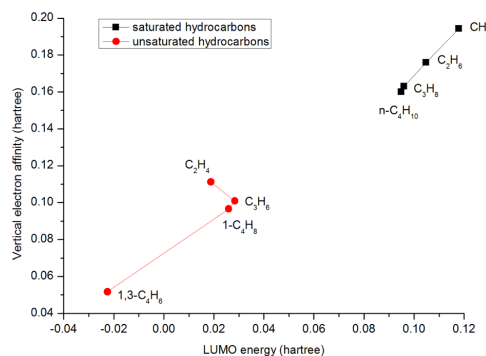


Fig.2 Vertical electron affinity and LUMO energy of hydrocarbons

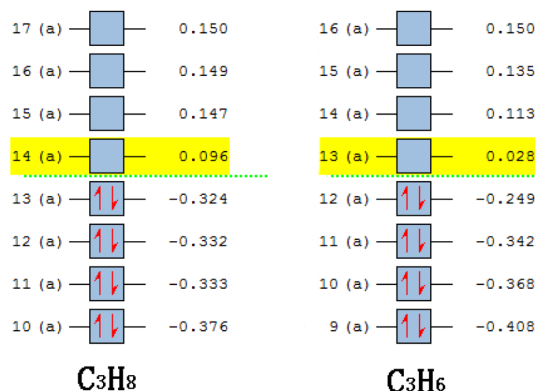


Fig.3 Molecule orbits distribution of C₃H₈ and C₃H₆

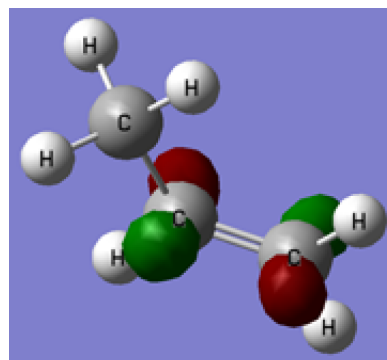


Fig.4 LUMO distribution of C₃H₆

Table 3 shows the vertical electron affinity of some saturated fluorocarbons. According to the experiment results by J. C. Devins, except CF_4 and CH_4 are close, the electric strengths of fluorocarbons are obviously better than hydrocarbons [27]. These trends of electric strengths and the vertical electron affinities are consistent with hydrocarbons. Fluorocarbons have low vertical electron affinity, which means better electron adsorption. The CF_4 and CH_4 are approximate in electric strength and vertical electron affinity, which also means that the insulation properties prediction cannot only rely on the element component such as fluorine, but also need specific analysis by vertical electron affinities and other microscopic data especially for non-polar molecules.

Table 3. Vertical electron affinity of saturated fluorocarbons

	Vertical electron affinity (Hartree)
Carbon-tetrafluoride (CF_4)	0.1473
Hexafluoroethane (C_2F_6)	0.0926
Octafluoropropane (C_3F_8)	0.0398

By the above analysis of organic gases with basis molecule structures, it can be obtained that the double bonds can reduce the energy of the electron unoccupied orbits, and for fluorocarbons, with the number of carbon atoms increasing, the vertical electron affinity can be reduced significantly. Unsaturated fluorocarbon molecules can match the two microscopic advantages. Table 4 shows the vertical electron affinities, LUMO energy, molecule volumes and relative electric strengths of unsaturated fluorocarbons [30]. Compared to the previous organic gases, unsaturated fluorocarbons vertical electron affinities are significantly lower and close to zero, even to be negative. In the B3LYP calculation method, with the lower vertical electron affinities, the tendency to absorb free electrons will be more obvious. So taking into account the impact of molecular volume, the calculation relative electric strength ES_r of molecules can be obtained as:

$$ES_r = a \cdot \log E_v + b \cdot S + c, \quad (3)$$

where the E_v is the vertical electron affinities, S is the physical sectional area of the molecules which can be calculated by molecule volume, and a , b and c are coefficients. Taking into account that the affinity E_v may possibly be a small negative value, the function can be changed as:

$$ES_r = a \cdot \log(E_v + d) + b \cdot S + c. \quad (4)$$

Table 4. Vertical electron affinities, LUMO energy, molecule volumes and relative electric strengths to SF_6 of unsaturated fluorocarbons

	Vertical electron affinity (Hartree)	LUMO energy (Hartree)	Molecule volume (Bohr^3)	Relative electric strength to SF_6 in DC uniform-field
1,3- C_4F_6	0.0239	-0.03425	783.914	1.5
2- C_4F_8	0.0051	-0.05137	900.815	1.75
2- C_4F_6	-0.0100	-0.03762	804.934	2.3

In this paper the ES_r is the calculation relative electric strength to nitrogen. For the above simple molecule structure organic gases, the coefficients can be $a = -2.7$, $b = 0.012$, $c = -1.6$, and $d = 0.03$. Fig. 5 is the calculation results and test results of the relative electric strength to nitrogen [27–29].

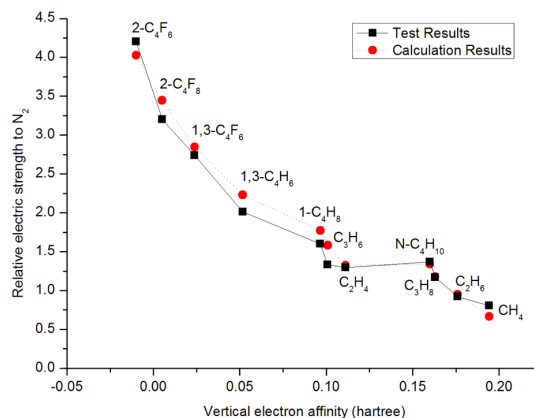
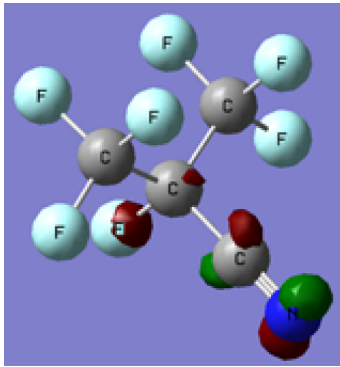
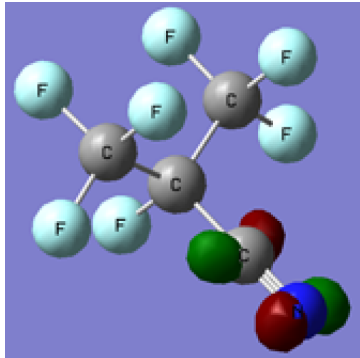
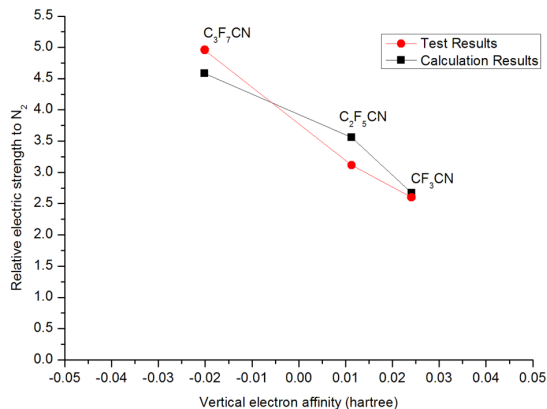


Fig.5 Calculation and test relative electric strength of hydrocarbons and fluorocarbons

In addition to the unsaturated fluorocarbons, fluoronitrile organic gases with triple bond ($\text{C}\equiv\text{N}$) also have good molecule properties including low vertical electron affinities, negative LUMO energy and large molecule size, as shown in Table 5. According to the above rules, these microscopic characteristics will bring good electrical performance. It is worth mentioning that $\text{C}\equiv\text{N}$ bond has dual low-energy unoccupied molecule orbits corresponding to two different distributions, which can make free electron absorption happen more easily, as shown in Fig. 6(a) and (b). Fig. 7 shows the test and calculation relative electric strength of fluoro-nitrile organic gases. According to J. C. Devins tests, the electric strength of fluoro-nitrile organic gases such as $\text{C}_3\text{F}_5\text{N}$ and 2- $\text{C}_4\text{F}_7\text{N}$ can be more than twice that of SF_6 [27]. Therefore, from the perspective of the test and microscopic calculation, the fluoro-nitrile structure can bring better electric strength than hydrocarbon and fluorocarbon with same number of carbon atoms.

Table 5. Vertical electron affinities, LUMO energy and molecule volumes of fluoro-nitriles

	Vertical electron affinity (Hartree)	LUMO energy (Hartree)	Molecule volume (Bohr^3)
2- $\text{C}_4\text{F}_7\text{N}$	-0.0201	-0.04707	932.985
$\text{C}_3\text{F}_5\text{N}$	0.0113	-0.03677	735.406
$\text{C}_2\text{F}_3\text{N}$	0.0241	-0.02788	522.360

(a) LUMO distribution with energy of -0.04707 Hartree(b) Second LUMO distribution with energy of -0.02240 Hartree**Fig.6** Unoccupied molecule orbitals distribution with negative energy of 2- C_4F_7N **Fig.7** Calculation and test relative electric strength of fluoro-nitrile gases

4 Conclusion

We have presented the microscopic research data of saturated and unsaturated hydrocarbon, fluorocarbon and fluoro-nitrile gases. The research shows that the vertical electron affinity and molecule volume of gas have correlations with the electric strength, which can be used to predict the relative electric strength by the calculating model and simplifying the screening for alternative gases. There must be other microscopic properties affecting the gas electric strength, so the calculating models in this paper still need further optimization and correction. The study also found that the vertical electron affinity is determined by the molecule structure

especially LUMO energy. For organic gas, the carbon double bonds can provide low energy LUMO and reduce the vertical electron affinity. So the unsaturated fluorocarbons have a good electrical strength theoretically which the experimental and calculating results of C_4F_8 and C_4F_6 have proved. On the other hand, fluoro-nitrile organic gases have good microscopic and electrical properties, but it is necessary to consider factors such as the boiling point and GWP value for industry application. The gases with a high boiling point and great electric strength can be used as mixed gases with nitrogen or other buffer gas, and the following research will focus on their toxicity and decomposition compounds.

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